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(72) OSTOJA STARZEWSKI, KARL-HEINZ ALEKSANDER, DE

(72) HOCH, MARTIN, DE

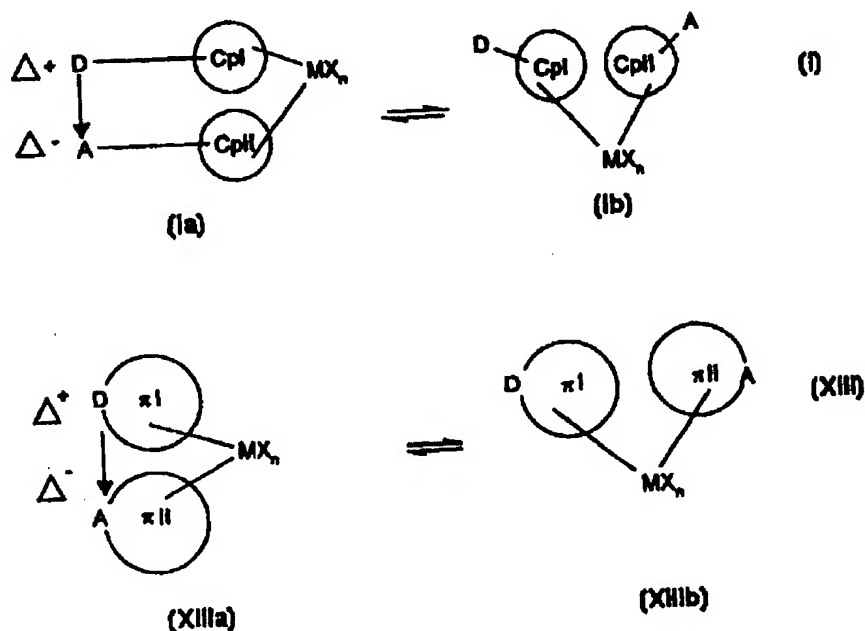
(71) BAYER AKTIENGESELLSCHAFT, DE

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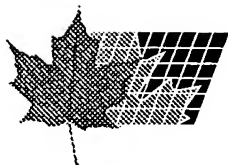
(54) **PROCEDE DE PRODUCTION D'ELASTOMERES**

(54) **METHOD FOR PRODUCING ELASTOMERS**



(57) Selon l'invention, des élastomères présentant, outre une structure amorphe et une basse température de transition vitreuse  $T_g$  mesurée par analyse calorimétrique différentielle, une cristallinité maximale à une température de fusion supérieure à + 40 °C, peuvent être produits par (co)polymérisation en masse, en solution, en solution à haute température, en suspension épaisse ou en phase gazeuse, de monomères du groupe des  $\alpha$ -oléfines  $C_2-C_8$ , des dioléfines  $C_4-C_{15}$ , ainsi que d'autres monomères. Les catalyseurs utilisés sont constitués de composés métallocènes ou de

(57) Elastomers with a crystallinity peak and melting temperature above 40 °C, in addition to having an amorphous structure and a low glass transition temperature  $T_g$  when measured according to DSC, can be produced by (co)polymerisation of monomers from the group of  $C_2-C_8$ - $\alpha$  olefins,  $C_4-C_{15}$  diolefins and other monomers in a mass, solution, high-temperature solution, slurry or gas phase, whereby metallocene compounds or cyclopentadienyl,  $\pi I$  and  $\pi II$  represent charged or complex compounds of formulae (I) or (XIII) are used, wherein  $CpI$  and  $CpII$  represent carbanion ions with a structure containing cyclopentadienyl,  $\pi I$  and  $\pi II$



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represent charged or composés de complexes .pi. de formules (I) ou (XIII), dans lesquelles CpI et CpII représentent des carbanions à structure comportant du cyclopentadiényl;  $\pi$ I et  $\pi$ II représentent des systèmes  $\pi$  chargés ou électriquement neutres; D représente un atome donneur, et A un atome accepteur; D et A sont liés par une liaison de coordination réversible de sorte que le groupe donneur accepte une charge (partielle) positive et le groupe accepteur accepte une charge (partielle) négative; M représente un métal de transition du sous-groupe III, IV, V ou VI de la classification périodique des éléments, y compris les lanthanides et les actinides; X représente un équivalent anionique et n, en fonction de la charge de M, vaut, 0, 1, 2, 3, ou 4.

electrically neutral cyclopentadienyl,  $\pi$ I and  $\pi$ II represent charged or systems, D is a donor atom and A is an acceptor atom, whereby D and A are linked by a reversible coordinate bond, the donor group accepts a positive (partial) charge and the acceptor group accepts a negative (partial charge), M stands for a transition metal of the periodic table of elements (Mendeleev) including the lathanoids and actinoids, and X is an anion equivalent representing the figure 0, 1, 2, 3 or 4, independent of the charge of M.

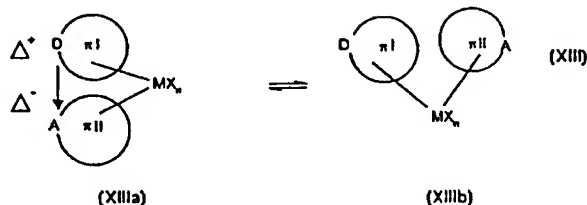
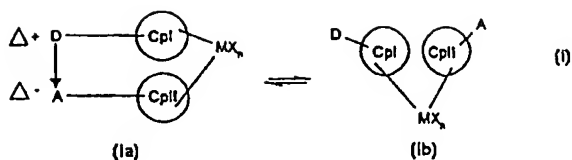


## (57) Abstract

Elastomers with a crystallinity peak and melting temperature above 40 °C, in addition to having an amorphous structure and a low glass transition temperature  $T_g$  when measured according to DSC, can be produced by (co)polymerisation of monomers from the group of  $C_2-C_8-\alpha$  olefins,  $C_4-C_{15}$  diolefins and other monomers in a mass, solution, high-temperature solution, slurry or gas phase, whereby metallocene compounds or  $\pi$  complex compounds of formulae (I) or (XIII) used, wherein CpI and CpII

represent carbanion ions with a structure containing cyclopentadienyl,  $\pi I$  and  $\pi II$  represent charged or electrically

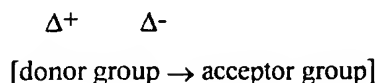
neutral  $\pi$  systems, D is a donor atom and A is an acceptor atom, whereby D and A are linked by a reversible coordinate bond, the donor group accepts a positive (partial) charge and the acceptor group accepts a negative (partial charge), M stands for a transition metal of the periodic table of elements (Mendeleev) including the lathanoids and actinoids, and X is an anion equivalent representing the figure 0, 1, 2, 3 or 4, independent of the charge of M.



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**Process for the preparation of elastomers**

The present invention relates to the use of  $\pi$  systems or metallocene compounds in which a transition metal is complexed with two  $\pi$  systems and especially with aromatic  $\pi$  systems such as anionic cyclopentadienyl ligands (carbanions), and the two systems are reversibly bonded together by at least one bridge consisting of a donor and an acceptor, as metal-organic catalysts in a process for the preparation of saturated or unsaturated elastomers which, in addition to the amorphous structure and a low glass transition temperature  $T_g$  in the DSC measurement (DSC = Differential Scanning Calorimetry), have a crystallinity peak with a melting temperature above  $+40^\circ\text{C}$ , by the (co)polymerization of monomers selected from the group consisting of  $\text{C}_2\text{-C}_8\text{-}\alpha$ -olefins, open-chain monocyclic and/or polycyclic  $\text{C}_4\text{-C}_{15}$ -diolefins and styrene. The coordinate bond formed between the donor atom and the acceptor atom produces a (partial) positive charge in the donor group and a (partial) negative charge in the acceptor group:



Metallocenes and their use as catalysts in the polymerization of olefins have been known for a long time (EP-A 129 368 and the literature cited therein). It is also known from EP-A 129 368 that metallocenes, in combination with alkylaluminium/ water as cocatalysts, are effective systems for the polymerization of ethylene (thus, for example, methylaluminoxane = MAO is formed from 1 mol of trimethyl-aluminium and 1 mol of water; other stoichiometric proportions have also already been used successfully (WO 94/20506)). Metallocenes whose cyclopentadienyl skeletons are covalently linked together by a bridge are already known as well. EP-A 704 461 may be mentioned as an example of the numerous patents and patent applications in this field: the linking group mentioned in said patent is a (substituted) methylene group or ethylene group, a silylene group, a substituted silylene group, a substituted germylene group or a substituted phosphine group. EP-A 704 461 also designates the bridged metallocenes as polymerization catalysts for olefins. Despite the numerous patents and

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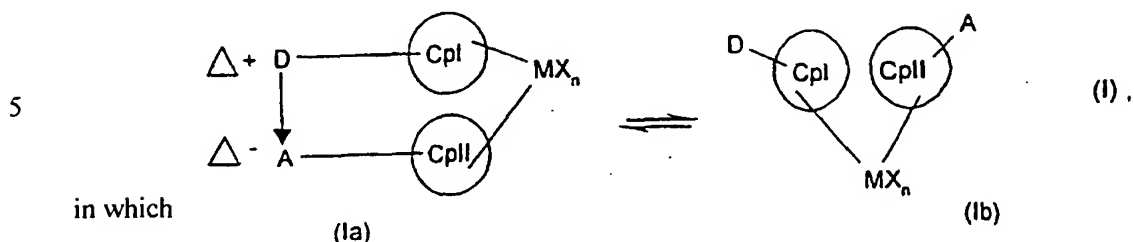
patent applications in this field, there is still a desire for improved catalysts which are distinguished by high activity, so that the amount of catalyst remaining in the polymer can be reduced, and which are suitable for example for the polymerization and copolymerization of olefins to thermoplasts and elastomeric products and for the  
5 polymerization and copolymerization of diolefins, optionally with olefins.

It has now been found that particularly advantageous catalysts can be prepared from bridged  $\pi$  complex compounds and especially metallocene compounds in which the bridging of the two  $\pi$  systems is created by one, two or three reversible donor-acceptor  
10 bonds, there being a coordinate or so-called dative bond between each donor atom and the corresponding acceptor atom, which bond is at least formally superimposed by an ionic bond, and it being possible for one of the donor or acceptor atoms to be part of its corresponding  $\pi$  system. The reversibility of the donor-acceptor bond allows not only the bridged state, characterized by the arrow between D and A, but also the unbridged  
15 state in which the two  $\pi$  systems, as a result of their inherent rotation energy, can rotate for example through 360 degrees relative to one another or deflect through a smaller angle and swing back again without destroying the integrity of the metal complex. After deflection or even complete rotation, the donor-acceptor bond "snaps in" again. If there are several donors and/or acceptors, this "snapping-in" can take place after  
20 rotation through less than 360 degrees.  $\pi$  systems to be used according to the invention, e.g. metallocenes, can therefore be represented by a double arrow and the partial formulae (Ia) and (Ib) or (XIIIa) and (XIIIb) in order to include both states.

The invention accordingly relates to a process for the preparation of saturated or  
25 unsaturated elastomers which, in addition to the amorphous structure and a low glass transition temperature  $T_g$  in the DSC measurement, have one or more melting peaks, at least one of which has its maximum at a melting temperature ( $T_m$ ) above  $+40^\circ\text{C}$ , preferably above  $50^\circ\text{C}$ , the half-intensity width of at least one melting peak preferably being at most  $30^\circ\text{C}$ , by the (co)polymerization of monomers selected from the group  
30 consisting of  $\text{C}_2$ - $\text{C}_8$ - $\alpha$ -olefins, open-chain monocyclic and/or polycyclic  $\text{C}_4$ - $\text{C}_{15}$ -diolefins and styrene, in the bulk, solution, high-temperature solution, slurry or gas phase, in the presence of metal-organic catalysts which can be activated by cocatalysts.

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which process is characterized in that the metal-organic catalysts used are metallocene compounds of the formula



CpI and CpII are two identical or different carbanions with a cyclopentadienyl-containing structure. in which one H atom to all the H atoms can be substituted by identical or different radicals selected from the group consisting of linear or branched C<sub>1</sub>-C<sub>20</sub>-alkyl which can be monosubstituted to fully substituted by halogen. monosubstituted to trisubstituted by phenyl and monosubstituted to trisubstituted by vinyl. C<sub>6</sub>-C<sub>12</sub>-aryl, halogenoaryl having 6 to 12 C atoms, and organometallic substituents such as silyl, trimethylsilyl or ferrocenyl, and can be monosubstituted or disubstituted by D and A,

D is a donor atom which can additionally carry substituents and which, in its particular bonding state, possesses at least one free electron pair,

20

A is an acceptor atom which can additionally carry substituents and which, in its particular bonding state, has an electron pair gap,

D and A being linked by a reversible coordinate bond in such a way that the donor group takes on a (partial) positive charge and the acceptor group a (partial) negative charge.

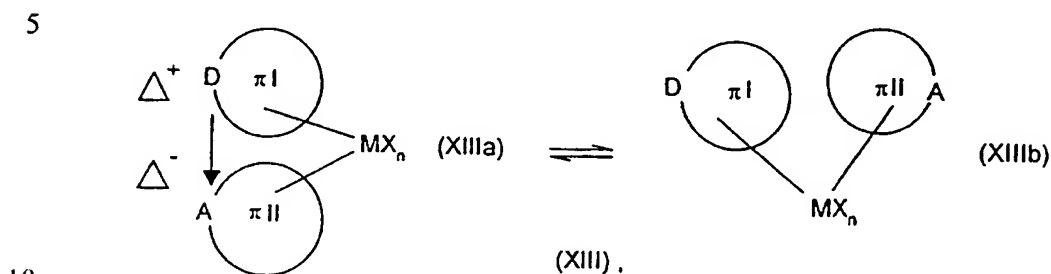
M is a transition metal of subgroup III, IV, V or VI of the periodic table of the elements (Mendeleev), including the lanthanides and actinides.

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X is one anion equivalent and

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n is the number zero, one, two, three or four, depending on the charge of M,  
or  $\pi$  complex compounds and especially metallocene compounds of the formula



in which

15  $\pi$ I and  $\pi$ II are different charged or electrically neutral  $\pi$  systems which can be fused with one or two unsaturated or saturated five-membered or six-membered rings,

20 D is a donor atom which is a substituent of  $\pi$ I or part of the  $\pi$  system of  $\pi$ I and which, in its particular bonding state, possesses at least one free electron pair,

A is an acceptor atom which is a substituent of  $\pi$ II or part of the  $\pi$  system of  $\pi$ II and which, in its particular bonding state, has an electron pair gap,

25 D and A being linked by a reversible coordinate bond in such a way that the donor group takes on a (partial) positive charge and the acceptor group a (partial) negative charge, and at least one of D and A being part of its corresponding  $\pi$  system,

it being possible for D and A in turn to carry substituents,

30 it being possible for each  $\pi$  system or each fused ring system to contain one or more D or A, or D and A, and

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it being possible, in  $\pi I$  and  $\pi II$  in the non-fused or in the fused form, for one H atom to all the H atoms of the  $\pi$  system to be substituted independently of one another by identical or different radicals selected from the group consisting of linear or branched  $C_1$ - $C_{20}$ -alkyl which can be monosubstituted to fully substituted by halogen, monosubstituted to trisubstituted by phenyl and monosubstituted to trisubstituted by vinyl,  $C_6$ - $C_{12}$ -aryl, halogenoaryl having 6 to 12 C atoms, and organometallic substituents such as silyl, trimethylsilyl and ferrocenyl, and to be monosubstituted or disubstituted by D and A, so that the reversible coordinate  $D \rightarrow A$  bond is formed (i) between D and A where they are both parts of the particular  $\pi$  system or the fused ring system, or (ii) between D and A where D or A is part of the  $\pi$  system or the fused ring system and the other one is a substituent of the non-fused  $\pi$  system or the fused ring system.

M and X are as defined above and

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n is the number zero, one, two, three or four, depending on the charges of M and those of  $\pi I$  and  $\pi II$ .

$\pi$  systems according to the invention are substituted and unsubstituted ethylene, allyl, pentadienyl, benzyl, butadiene, benzene, the cyclopentadienyl anion and the species obtained by replacing at least one C atom with a heteroatom. Of said species, those which are cyclic are preferred. The nature of the coordination of such ligands ( $\pi$  systems) to the metal can be of the  $\sigma$  type or of the  $\pi$  type.

Such metallocene compounds of formula (I) to be used according to the invention can be prepared either by reacting a compound of formula (II) with a compound of formula (III):

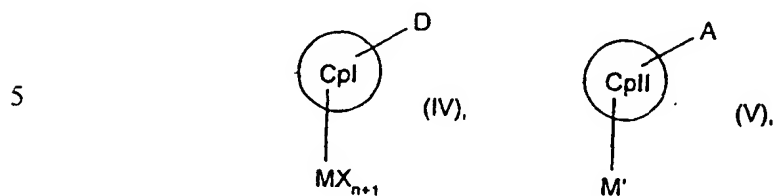
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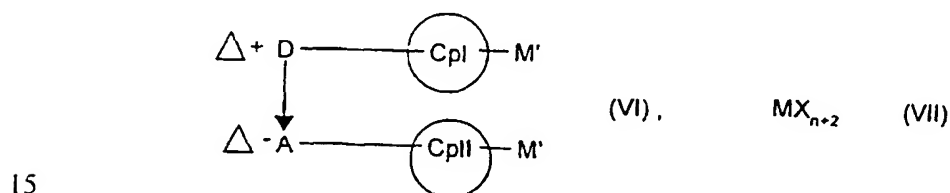


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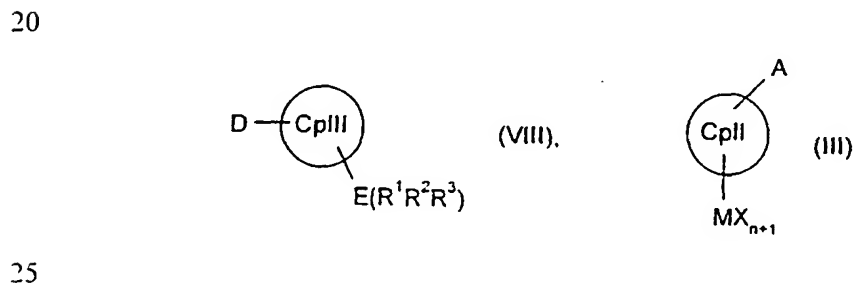
or by reacting a compound of formula (IV) with a compound of formula (V):



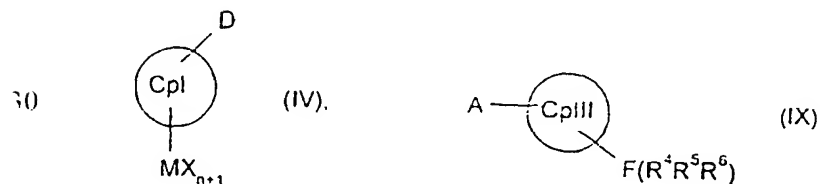
10 or by reacting a compound of formula (VI) with a compound of formula (VII):



with the elimination of  $M'X$ , in the presence of an aprotic solvent, or by reacting a compound of formula (VIII) with a compound of formula (III):

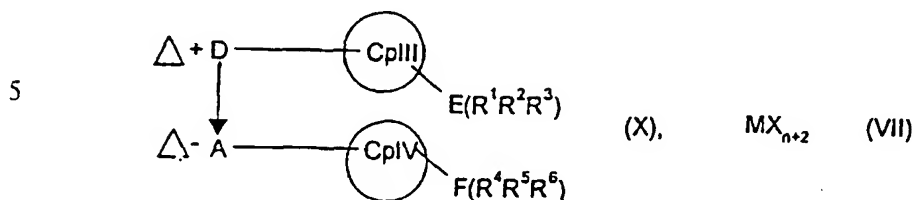


or by reacting a compound of formula (IV) with a compound of formula (IX):



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or by reacting a compound of formula (X) with a compound of formula (VII):



- 10 with the elimination of  $E(R^1R^2R^3)X$  and  $F(R^4R^5R^6)X$ , in the absence or presence of an aprotic solvent.

Cpl, CplI, D, A, M, X and n being as defined above,

- 15 CplIII and CplIV being two identical or different uncharged molecular moieties with a cyclopentadiene-containing structure, but otherwise being identical to CplI and CplII,

M' being one cation equivalent of an alkali (alkaline earth) metal or Tl,

- 20 E and F independently of one another being one of the elements Si, Ge or Sn and

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  independently of one another being linear or branched  $C_1$ - $C_{20}$ -alkyl,  $C_6$ - $C_{12}$ -aryl,  $C_1$ - $C_6$ -alkyl- $C_6$ - $C_{12}$ -aryl,  $C_6$ - $C_{12}$ -aryl- $C_1$ - $C_6$ -alkyl, vinyl, allyl or halogen.

25

- it also being possible, in formulae (VIII), (IX) and (X), for  $E(R^1R^2R^3)$  and  $F(R^4R^5R^6)$  to be replaced with hydrogen, in which case X can also be an amide anion of the type  $R_2N^-$ , a carbanion of the type  $R_3C^-$  or an alcoholate anion of the type  $RO^-$ , and it also being possible to react compounds of formula (II) or (VIII) directly with a transition metal compound of formula (VII) in the presence of compounds of formula (V) or (IX).
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In the reaction of (VIII) with (III), (IV) with (IX) or (X) with (VII), the structure (I) is formed, in the case of the last-mentioned variant, with the elimination of an amine  $R_2NH$ ,  $R_2NE(R^1R^2R^3)$  or  $R_2NF(R^4R^5R^6)$ , a hydrocarbon compound of the formula  $R_3CH$ ,  $R_3CE(R^1R^2R^3)$  or  $R_3CF(R^4R^5R^6)$ , or an ether  $ROE(R^1R^2R^3)$  or  $ROF(R^4R^5R^6)$ ,  
 5 wherein the organic radicals R are identical or different and independently of one another are  $C_1$ - $C_{20}$ -alkyl,  $C_6$ - $C_{12}$ -aryl, substituted or unsubstituted allyl, benzyl or hydrogen. Possible examples of the eliminated amine, hydrocarbon, ether, silane, stannane or germane are dimethylamine, diethylamine, di(n-propyl)amine, di-(isopropyl)amine, di(tert-butyl)amine, tert-butylamine, cyclohexylamine, aniline,  
 10 methylphenylamine, di(allyl)amine, methane, toluene, trimethylsilylamine, trimethylsilyl ether, tetramethylsilane, hexamethyldisilazane etc.

It is also possible to react compounds of formula (II) or (VIII) directly with a transition metal compound of formula (VII) in the presence of compounds of formula (V) or  
 15 (IX).

$\pi$  complex compounds of formula (XIII) in which the  $\pi$  systems are cyclic and aromatic (metallocenes) can be prepared by analogy using the following compounds as appropriate:

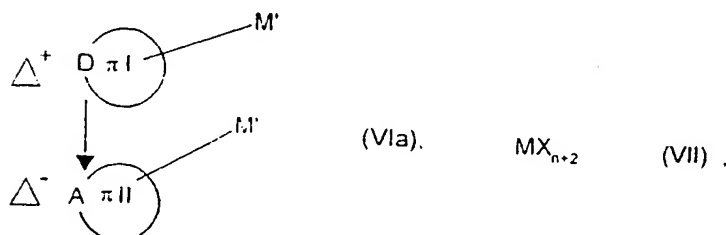
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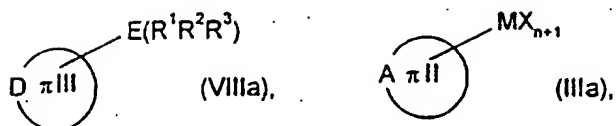
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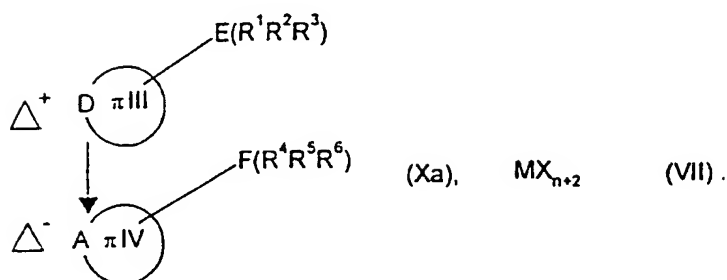
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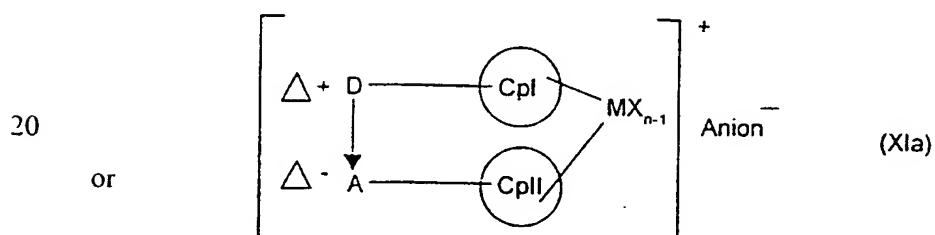
Non-cyclic  $\pi$  complex compounds are prepared by the processes known to those skilled in the art, with the incorporation of donor and acceptor groups.

According to the invention, the polymerization is carried out in the bulk, solution, high-temperature solution, slurry or gas phase at  $-60$  to  $250^{\circ}\text{C}$ , preferably  $0$  to  $+200^{\circ}\text{C}$ , and  $1$  to  $65$  bar, in the presence or absence of saturated or aromatic hydrocarbons or saturated or aromatic halogenohydrocarbons and in the presence or absence of hydrogen, the metallocene compounds or  $\pi$  complex compounds being used as catalysts in an amount of  $10^1$  to  $10^{12}$  mol of all monomers per mol of metallocene or  $\pi$  complex compounds, it also being possible for the polymerization to be carried out in the presence of Lewis acids, Brönsted acids or Pearson acids or additionally in the presence of Lewis bases.

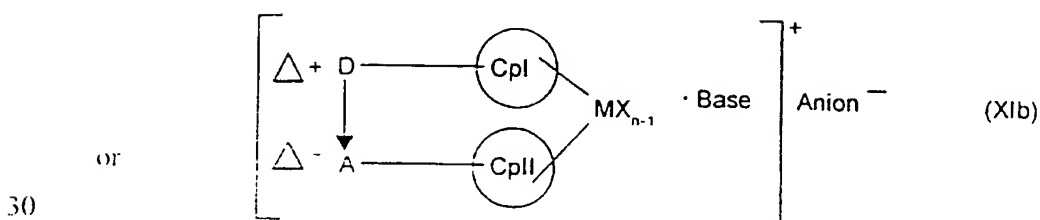
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- Examples of such Lewis acids are boranes or alanes such as alkylaluminium compounds, aluminium halides, aluminium alcoholates, organoboron compounds, boron halides, boric acid esters or boron and aluminium compounds containing both halide and alkyl, aryl or alcoholate substituents, as well as mixtures thereof, or the triphenylmethyl cation. Aluminoxanes or mixtures of aluminium-containing Lewis acids with water are particularly preferred. According to current knowledge, all acids work as ionizing agents to form a metallocenium cation which is charge-compensated by a bulky, poorly coordinating anion.
- According to the invention, it is also possible to use the reaction products of such ionizing agents with metallocene compounds of formula (I) or  $\pi$  complex compounds of formula (XIII). They can be described by formulae (XIa) to (XIId):

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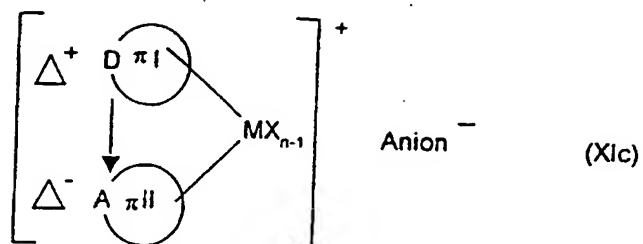


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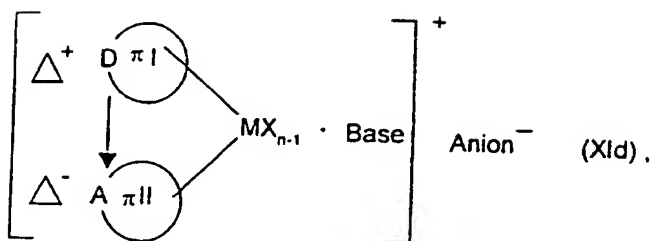
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or

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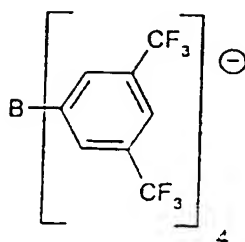
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in which

20 Anion represents the entire bulky, poorly coordinating anion and Base represents a Lewis base.

Examples of such poorly coordinating anions are  $B(C_6H_5)_4$ ,  $B(C_6F_5)_4$ ,  $B(CH_3)(C_6F_5)_3$ .

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sulfonates such as tosylate or triflate, tetrafluoroborates, hexafluorophosphates, hexafluoroantimonates, perchlorates and bulky cluster molecular anions of the carborane type, for example  $C_2B_9H_{12}^-$  or  $CB_{11}H_{12}^-$ . When such anions are present, metallocene compounds can also work as high-efficiency polymerization catalysts in the absence of

5 aluminoxane. This is the case particularly when one X ligand is an alkyl group, allyl or benzyl. It can also be advantageous, however, to use such metallocene complexes with bulky anions in combination with alkylaluminium compounds such as  $(CH_3)_3Al$ ,  $(C_2H_5)_3Al$ ,  $(n\text{-}i\text{-propyl})_3Al$ ,  $(n\text{-}t\text{-butyl})_3Al$ ,  $(i\text{-butyl})_3Al$  or the isomeric pentyl-, hexyl- or octyl-aluminium compounds, alkyl lithium compounds such as methyl-Li, benzyl-Li

10 or butyl-Li, or the corresponding organomagnesium compounds such as Grignard compounds, or organozinc compounds. On the one hand such metal alkyls transfer alkyl groups to the central metal, and on the other hand they trap water or catalyst poisons from the reaction medium or monomer during polymerization reactions. Metal alkyls of the type described can also advantageously be used in combination

15 with aluminoxane cocatalysts, for instance to reduce the required amount of aluminoxane. Such anions are introduced when using e.g. the following boron compounds:

triethylammonium tetraphenylborate,

20 tripropylammonium tetraphenylborate,

tri(n-butyl)ammonium tetraphenylborate,

tri(t-butyl)ammonium tetraphenylborate,

N,N-dimethylanilinium tetraphenylborate,

N,N-diethylanilinium tetraphenylborate,

25 N,N-dimethyl(2,4,6-trimethylanilinium) tetraphenylborate,

trimethylammonium tetrakis(pentafluorophenyl)borate, triethylammonium

tetrakis(pentafluorophenyl)borate,

tripropylammonium tetrakis(pentafluorophenyl)borate,

tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, tri(sec-butyl)ammonium

30 tetrakis(pentafluorophenyl)borate,

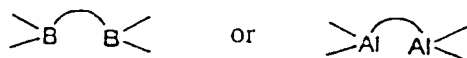
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate.

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- N,N-diethylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl(2,4,5-trimethylanilinium) tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate, triethylammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate,
- 5 tripropylammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate, dimethyl(t-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate, N,N-dimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl)borate, N,N-diethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl)borate and
- 10 N,N-dimethyl(2,4,6-trimethylanilinium) tetrakis(2,3,4,6-tetrafluorophenyl)borate: dialkylammonium salts such as: di(i-propyl)ammonium tetrakis(pentafluorophenyl)borate and dicyclohexylammonium tetrakis(pentafluorophenyl)borate; trisubstituted phosphonium salts such as:
- 15 triphenylphosphonium tetrakis(pentafluorophenyl)borate, tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate; tritolylmethyl tetrakis(pentafluorophenyl)borate; triphenylmethyl tetraphenylborate (trityl tetraphenylborate);
- 20 trityl tetrakis(pentafluorophenyl)borate; silver tetrafluoroborate; tris(pentafluorophenyl)borane; tris(trifluoromethyl)borane; and the analogous Al compounds.
- 25 Further alternative possibilities are fluorinated but otherwise analogous boron and aluminium compounds having 1 to 3 fluorine substituents.

Other poorly coordinating anions can be formed from diboranyl or dialanyl compounds of the type

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The metallocene compounds or  $\pi$  complex compounds to be used according to the invention can be employed for the (co)polymerization in the isolated form as pure substances, but they can also be produced and used "in situ" in the (co)polymerization reactor in a manner known to those skilled in the art.

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The first and second carbanions CpI and CpII with a cyclopentadienyl skeleton, or  $\pi$ I and  $\pi$ II if they represent a cyclopentadienyl skeleton, can be identical or different. The cyclopentadienyl skeleton can be for example a skeleton selected from the group consisting of cyclopentadiene, substituted cyclopentadiene, indene, substituted indene, fluorene and substituted fluorene. There may be 1 to 4 substituents per cyclopentadiene ring or fused benzene ring. These substituents can be C<sub>1</sub>-C<sub>20</sub>-alkyl such as methyl, ethyl, propyl, isopropyl, butyl or isobutyl, hexyl, octyl, decyl, dodecyl, hexadecyl, octadecyl or eicosyl, C<sub>1</sub>-C<sub>20</sub>-alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy or isobutoxy, hexyloxy, octyloxy, decyloxy, dodecyloxy, hexadecyloxy, octadecyloxy or eicosyloxy, halogen such as fluorine, chlorine or bromine, C<sub>6</sub>-C<sub>12</sub>-aryl such as phenyl, C<sub>1</sub>-C<sub>4</sub>-alkylphenyl such as tolyl, ethylphenyl, (i-)propylphenyl, (i-/tert-)butylphenyl or xylyl, halogenophenyl such as fluorophenyl, chlorophenyl or bromophenyl, naphthyl or biphenyl, triorganosilyl such as trimethylsilyl (TMS), ferrocenyl, or D or A, as defined above. Fused aromatic rings can also be partially or completely hydrogenated so that the only remaining double bond is the one to which both the fused ring and the cyclopentadiene ring contribute. Benzene rings can also contain one or two additional fused benzene rings, as in indene or fluorene. It is further possible for the cyclopentadiene ring or cyclopentadienyl ring and a fused benzene ring together to contain another fused benzene ring.

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In the form of their anions, such cyclopentadiene skeletons are excellent ligands for transition metals, each cyclopentadienyl carbanion of said optionally substituted form compensating one positive charge of the central metal in the complex. Specific examples of such carbanions are: cyclopentadienyl, methylcyclopentadienyl, 1,2-dimethylcyclopentadienyl, 1,3-dimethylcyclopentadienyl, indenyl, phenylindenyl, 1,2-diethylcyclopentadienyl, tetramethylcyclopentadienyl, ethylcyclopentadienyl, n-butylcyclopentadienyl, n-octylcyclopentadienyl,  $\beta$ -phenylpropylcyclopentadienyl, tetra-

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hydroindenyl, propylcyclopentadienyl, t-butylcyclopentadienyl, benzylcyclopentadienyl, diphenylmethylcyclopentadienyl, trimethylgermylcyclopentadienyl, trimethylstannylcyclopentadienyl, trifluoromethylcyclopentadienyl, trimethylsilyl-cyclopentadienyl, pentamethylcyclopentadienyl, fluorenyl, tetrahydro- or octahydro-fluorenyl, fluorenyls and indenyls benzo-fused on the six-membered ring, N,N-dimethylaminocyclopentadienyl, dimethylphosphinocyclopentadienyl, methoxycyclopentadienyl, dimethylboranylcyclopentadienyl and (N,N-dimethylaminomethyl)-cyclopentadienyl.

In addition to the first donor-acceptor bond between D and A, which must be present, other donor-acceptor bonds can be formed if additional D and/or A groups are present as substituents of the particular cyclopentadiene systems or as substituents or parts of the  $\pi$  systems. All donor-acceptor bonds are characterized by their reversibility, as described above. If there are several D or A groups, these can occupy different positions among those mentioned. The invention accordingly covers both the bridged molecular states (Ia) or (XIIIa) and the unbridged states (Ib) or (XIIIb). The number of D groups can be identical to or different from the number of A groups. CpI and CpII or  $\pi$ I and  $\pi$ II are preferably linked via only one donor-acceptor bridge.

Covalent bridges can also be present as well as the D/A bridges according to the invention. In this case, the D/A bridges reinforce the stereorigidity and the thermal stability of the catalyst. As the D/A bond changes between closed and open, block polymers become obtainable in the case of copolymers with different chemical compositions.

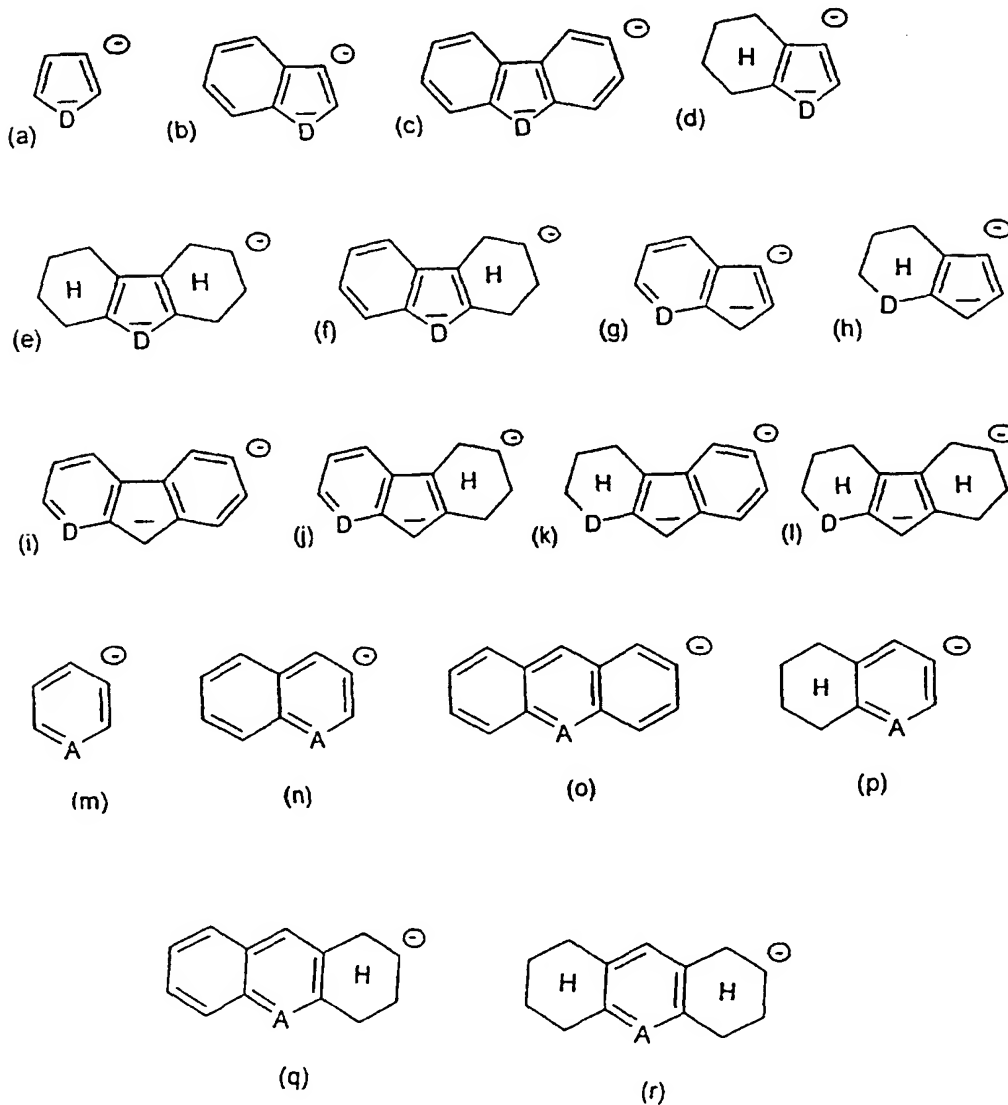
The  $\pi$  complex compounds are also characterized by the presence of at least one coordinate bond between the donor atom(s) D and the acceptor atom(s) A. Here, both D and A can be substituents of their corresponding  $\pi$  system  $\pi$ I or  $\pi$ II or part of the  $\pi$  system, although at least one of D and A is always part of the  $\pi$  system.  $\pi$  system is understood here as meaning the entire  $\pi$  system, optionally fused with one or two rings. This results in the following embodiments:

- D is part of the  $\pi$  system. A is a substituent of the  $\pi$  system;

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- D is a substituent of the  $\pi$  system, A is part of the  $\pi$  system;
- D and A are parts of their corresponding  $\pi$  system.

The following may be mentioned as examples of heterocyclic ring systems in which D or A is part of the ring system:



Important heterocyclic ring systems are the systems denoted by (a), (b), (c), (d), (g), (m), (n) and (o); those denoted by (a), (b), (c) and (m) are particularly important.

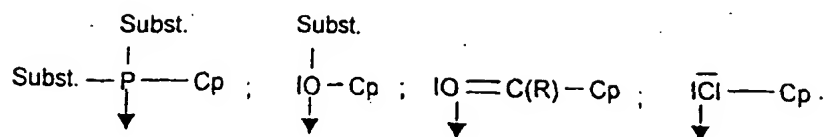
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In the case where one of D and A is a substituent of its corresponding ring system, the latter is 3-, 4-, 5-, 6-, 7- or 8-membered, with or without electrical charge, and can be further substituted and/or fused in the manner indicated. 5-membered and 6-membered ring systems are preferred. The negatively charged cyclopentadienyl system is particularly preferred.

If it is in the form of a ring system, the first or second  $\pi$  system  $\pi I$  or  $\pi II$  can correspond to CpI or CpII in the case where one of D and A is a substituent of the ring system.

Possible donor groups are especially those in which the donor atom D is an element of main group 5, 6 or 7, preferably 5 or 6, of the periodic table of the elements (Mendeleeff) and possesses at least one free electron pair, and in which the donor atom is in a bonding state with substituents in the case of elements of main group 5 and can be in such a state in the case of elements of main group 6; donor atoms of main group 7 carry no substituents. This is illustrated below using phosphorus, P, oxygen, O, and chlorine, Cl, as examples of donor atoms, "Subst." representing said substituents and "-Cp" representing the bond to the cyclopentadienyl-containing carbanion, a line with an arrow denoting a coordinate bond as indicated in formula (I), and other lines representing available electron pairs:

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Possible acceptor groups are especially those in which the acceptor atom A is an element of main group 3 of the periodic table of the elements (Mendeleeff), such as boron, aluminium, gallium, indium or thallium, is in a bonding state with substituents and possesses an electron gap.

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D and A are linked by a coordinate bond, D taking on a (partial) positive charge and A a (partial) negative charge.

A distinction is thus made between the donor atom D and the donor group and between the acceptor atom A and the acceptor group. The coordinate bond D→A is created between the donor atom D and the acceptor atom A. The donor group is the unit comprising the donor atom D, the substituents, if present, and the available electron pairs; by analogy, the acceptor group is the unit comprising the acceptor atom A, the substituents and the available electron gap.

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The bond between the donor atom or the acceptor atom and the cyclopentadienyl-containing carbanion can be interrupted by spacer groups to give D-Spacer-Cp or A-Spacer-Cp. In the third of the above examples of formulae, =C(R)- represents such a spacer between O and Cp. Examples of such spacer groups are:

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dimethylsilyl, diethylsilyl, di-n-propylsilyl, diisopropylsilyl, di-n-butylsilyl, di-t-butylsilyl, di-n-hexylsilyl, methylphenylsilyl, ethylmethylsilyl, diphenylsilyl, di(p-t-butylphenethylsilyl), n-hexylmethylsilyl, cyclopentamethylenesilyl, cyclotetramethylenesilyl, cyclotrimethylenesilyl, dimethylgermanyl, diethylgermanyl, phenylamino, t-butylamino, methylamino, t-butylphosphino, ethylphosphino, phenylphosphino, methylene, dimethylmethylene (i-propylidene), diethylmethylene, ethylene, dimethylethylene, diethylethylene, dipropylethylene, propylene.

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dimethylpropylene, diethylpropylene, 1,1-dimethyl-3,3-dimethylpropylene, tetramethyldisiloxane, 1,1,4,4-tetramethyldisilylethylene and diphenylmethylenes.

- 5 Preferably, D and A are bonded without spacers to the cyclopentadienyl-containing carbanion.

D and A can be located, independently of one another, on the cyclopentadiene (cyclopentadienyl) ring, or a fused benzene ring or fused heterocycle, or another  
10 substituent of Cpl or CpII or  $\pi I/\pi II$ . Where there are several D or A groups, these can occupy different positions among those mentioned.

Examples of substituents on the donor atoms N, P, As, Sb, Bi, O, S, Se or Te and on the acceptor atoms B, Al, Ga, In or Tl are: C<sub>1</sub>-C<sub>12</sub>-(cyclo)alkyl such as methyl, ethyl,  
15 propyl, i-propyl, cyclopropyl, butyl, i-butyl, tert-butyl, cyclobutyl, pentyl, neopentyl, cyclopentyl, hexyl, cyclohexyl and the isomeric heptyls, octyls, nonyls, decyls, undecyls and dodecyls; the corresponding C<sub>1</sub>-C<sub>12</sub>-alkoxy groups; vinyl, butenyl and allyl; C<sub>6</sub>-C<sub>12</sub>-aryl such as phenyl, naphthyl or biphenyl, and benzyl, which can be substituted by halogen, 1 or 2 C<sub>1</sub>-C<sub>4</sub>-alkyl groups, C<sub>1</sub>-C<sub>4</sub>-alkoxy groups, nitro or  
20 halogenoalkyl groups, C<sub>1</sub>-C<sub>6</sub>-alkylcarboxyl, C<sub>1</sub>-C<sub>6</sub>-alkylcarbonyl or cyano (e.g. perfluorophenyl, m,m'-bis(trifluoromethyl)phenyl and analogous substituents familiar to those skilled in the art); analogous aryloxy groups; indenyl; halogen such as F, Cl, Br and I; 1-thienyl; disubstituted amino such as (C<sub>1</sub>-C<sub>12</sub>-alkyl)<sub>2</sub>amino, diphenylamino, (C<sub>1</sub>-C<sub>12</sub>-alkyl)(phenyl)amino and (C<sub>1</sub>-C<sub>12</sub>-alkylphenyl)amino; tris(C<sub>1</sub>-C<sub>12</sub>-alkyl)silyl;  
25 NaSO<sub>3</sub>-aryl such as NaSO<sub>3</sub>-phenyl and NaSO<sub>3</sub>-tolyl; C<sub>6</sub>H<sub>5</sub>-C $\equiv$ C-; aliphatic and aromatic C<sub>1</sub>-C<sub>20</sub>-silyl whose alkyl substituents can be octyl, decyl, dodecyl, stearyl or eicosyl, in addition to those mentioned above, and whose aryl substituents can be phenyl, tolyl, xylyl, naphthyl or biphenyl; and substituted silyl groups which are bonded via -CH<sub>2</sub>- to the donor atom or acceptor atom, for example (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>-; C<sub>n</sub>-  
30 C<sub>12</sub>-aryloxy containing the above-mentioned aryl groups; C<sub>1</sub>-C<sub>8</sub>-perfluoroalkyl; and perfluorophenyl. Preferred substituents are C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>5</sub>-C<sub>6</sub>-cycloalkyl, phenyl,

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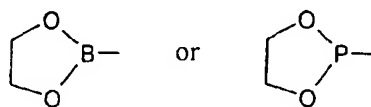
tolyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>6</sub>-C<sub>12</sub>-aryloxy, vinyl, allyl, benzyl, perfluorophenyl, F, Cl, Br, di(C<sub>1</sub>-C<sub>6</sub>-alkyl)amino and diphenylamino.

Donor groups are groups in which the free electron pair is located on N, P, As, Sb, Bi, O, S, Se, Te, F, Cl, Br or I, the preferred atoms being N, P, O and S. Examples of donor groups which may be mentioned are: (CH<sub>3</sub>)<sub>2</sub>N-, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N-, (C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>N-, (C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>N-, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>N-, (CH<sub>3</sub>)<sub>2</sub>P-, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>P-, (C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>P-, (i-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>P-, (C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>P-, (t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>P-, (cyclohexyl)<sub>2</sub>P-, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P-, CH<sub>3</sub>O-, CH<sub>3</sub>S-, C<sub>6</sub>H<sub>5</sub>S-, -C(C<sub>6</sub>H<sub>5</sub>)=O, -C(CH<sub>3</sub>)=O, -OSi(CH<sub>3</sub>)<sub>3</sub> and -OSi(CH<sub>3</sub>)<sub>2</sub>-t-butyl, in which N and P each carry one free electron pair and O and S each carry two free electron pairs, and in which the double-bonded oxygen in the last two examples mentioned is bonded via a spacer group, as well as systems, like the pyrrolidone ring, where the ring members which are different from N also act as spacers.

Acceptor groups are groups in which an electron pair gap is present on B, Al, Ga, In or Tl, preferably B, Al or Ga; examples which may be mentioned are: (CH<sub>3</sub>)<sub>2</sub>B-, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>B-, H<sub>2</sub>B-, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>B-, (CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)B-, (vinyl)<sub>2</sub>B-, (benzyl)<sub>2</sub>B-, Cl<sub>2</sub>B-, (CH<sub>3</sub>O)<sub>2</sub>B-, Cl<sub>2</sub>Al-, (CH<sub>3</sub>)Al-, (i-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Al-, (Cl)(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Al-, (CH<sub>3</sub>)<sub>2</sub>Ga-, (C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>Ga-, ((CH<sub>3</sub>)<sub>3</sub>Si-CH<sub>2</sub>)<sub>2</sub>Ga-, (vinyl)<sub>2</sub>Ga-, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Ga-, (CH<sub>3</sub>)<sub>2</sub>In-, ((CH<sub>3</sub>)<sub>3</sub>Si-CH<sub>2</sub>)<sub>2</sub>In- and (cyclopentadienyl)<sub>2</sub>In-. Of said species, other possibilities are those in which 1 or more H atoms are replaced with fluorine.

Other possible donor and acceptor groups are those which contain chiral centres or in which 2 substituents form a ring with the D or A atom, possible examples being

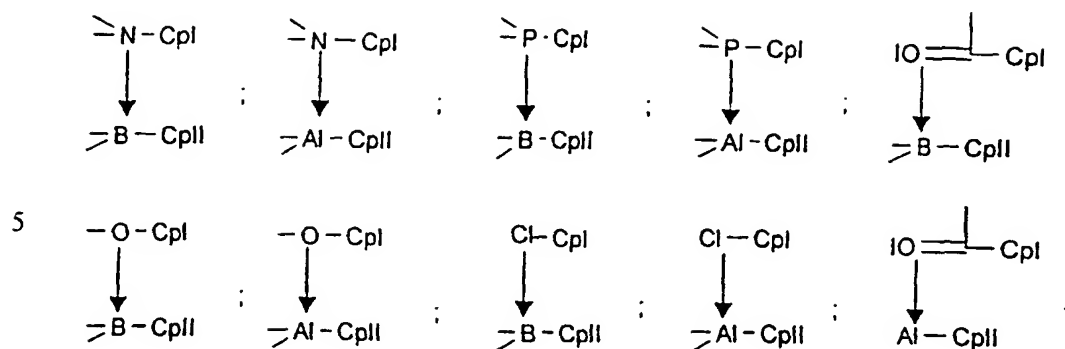
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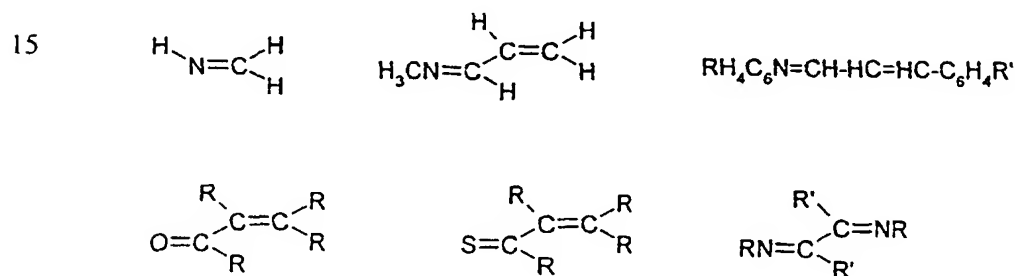
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The following are examples of preferred donor-acceptor bridges between Cpl and CplI:

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One or both of the  $\pi$  systems  $\pi I$  and  $\pi II$  can be present as a heterocycle in the form of the above ring systems (a) to (r). In this case, D is preferably an element of main group 5 or 6 of the periodic table of the elements (Mendeleeff) and A is preferably boron. Specific examples of such hetero  $\pi$  systems, especially heterocycles, are:



R, R' = H, alkyl, aryl or alkaryl, e.g. methyl, ethyl, t-butyl, phenyl or o,o'-di(i-propyl)phenyl

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Examples of heterocycles are: pyrrolyl, methylpyrrolyl, dimethylpyrrolyl, trimethylpyrrolyl, tetramethylpyrrolyl, t-butylpyrrolyl, di-t-butylpyrrolyl, indolyl, methylindolyl, dimethylindolyl, t-butylindolyl, di-t-butylindolyl, tetramethylphospholyl, tetraphenylphospholyl, triphenylphospholyl, trimethylphospholyl, phosphaindenyl, dibenzophospholyl (phosphafluorenyl) and dibenzopyrrolyl.

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The following are examples of preferred donor-acceptor bridges between  $\pi I$  and  $\pi II$ :  $N \rightarrow B$ ,  $N \rightarrow Al$ ,  $P \rightarrow B$ ,  $P \rightarrow Al$ ,  $O \rightarrow B$ ,  $O \rightarrow Al$ ,  $Cl \rightarrow B$ ,  $Cl \rightarrow Al$ ,  $C=O \rightarrow B$  and  $C=O \rightarrow Al$ , it being possible for both atoms of these donor-acceptor bridges to be part of a hetero  $\pi$  system, or one atom (donor or acceptor) being part of a  $\pi$  system and the other being a substituent of the second  $\pi$  system, or both atoms being substituents of their particular rings and one of the rings additionally containing a heteroatom.

According to the above description, the two ligand systems  $\pi I$  and  $\pi II$  can be linked by one, two or three donor-acceptor bridges. This is possible because, according to the invention, formula (Ia) contains the described  $D \rightarrow A$  bridge but the ligand systems  $\pi I$  and  $\pi II$  can also carry other D and A groups as substituents or hetero  $\pi$  centres; the number of additional  $D \rightarrow A$  bridges resulting from this is zero, one or two. The number of D or A substituents on  $\pi I$  or  $\pi II$  can be identical or different. The two ligand systems  $\pi I$  and  $\pi II$  can additionally be covalently bridged. (Examples of covalent bridges are described above as spacer groups.) Preferred compounds, however, are those which do not have a covalent bridge and in which  $\pi I$  and  $\pi II$  are accordingly linked via only one donor-acceptor bridge.

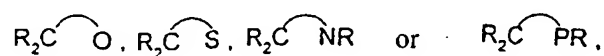
M is a transition metal of subgroup 3, 4, 5 or 6 of the periodic table of the elements (Mendeleeff), including the lanthanides and actinides; examples which may be mentioned are: Sc, Y, La, Sm, Nd, Lu, Ti, Zr, Hf, Th, V, Nb, Ta and Cr. Ti, Zr, Hf, V and Nb are preferred.

In the formation of the metallocene structure or the  $\pi$  complex structure, one positive charge of the transition metal M is compensated by one cyclopentadienyl-containing carbanion. Positive charges still remaining on the central atom M are neutralized by other, mostly monovalent anions X, it also being possible for two identical or different anions X to be linked together (dianions  $x \quad x$ ), for example singly or doubly charged negative radicals made up of identical or different, linear or branched, saturated or unsaturated hydrocarbons, amines, phosphines, thioalcohols, alcohols or phenols. Monoanions, such as  $CR_3^-$ ,  $NR_2^-$ ,  $PR_2^-$ ,  $OR^-$ ,  $SR^-$  etc., can be joined together by saturated or unsaturated hydrocarbon or silane bridges to form dianions, and the

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number of bridging atoms can be 0, 1, 2, 3, 4, 5 or 6, 0 to 4 bridging atoms being preferred and 1 or 2 bridging atoms being particularly preferred. Apart from H atoms, the bridging atoms can also carry further hydrocarbon substituents R. Possible examples of bridges between the monoanions are -CH<sub>2</sub>-, -CH<sub>2</sub>-CH<sub>2</sub>-, -(CH<sub>2</sub>)<sub>3</sub>-, -CH=CH-, -(CH=CH)<sub>2</sub>-, -CH=CH-CH<sub>2</sub>-, -CH<sub>2</sub>-CH=CH-CH<sub>2</sub>-, -Si(CH<sub>3</sub>)<sub>2</sub>- and -C(CH<sub>3</sub>)<sub>2</sub>-. Examples of X are: hydride, chloride, methyl, ethyl, phenyl, fluoride, bromide, iodide, the n-propyl radical, the i-propyl radical, the n-butyl radical, the amyl radical, the i-amyl radical, the hexyl radical, the i-butyl radical, the heptyl radical, the octyl radical, the nonyl radical, the decyl radical, the cetyl radical, methoxy, ethoxy, propoxy, butoxy, phenoxy, dimethylamino, diethylamino, methylethylamino, di-  
 5 butylamino, diphenylamino, diphenylphosphino, dicyclohexylphosphino, dimethylphosphino, methylidene, ethylidene, propylidene and the ethylene glycol dianion. Examples of dianions are 1,4-diphenyl-1,3-butadienediyl, 3-methyl-1,3-pentadienediyl, 1,4-dibenzyl-1,3-butadienediyl, 2,4-hexadienediyl, 1,3-pentadienediyl, 1,4-ditolyl-1,3-butadienediyl, 1,4-bis(trimethylsilyl)-1,3-butadienediyl and 1,3-butadienediyl. 1,4-Diphenyl-1,3-butadienediyl, 1,3-pentadienediyl, 1,4-dibenzyl-1,3-butadienediyl, 2,4-hexadienediyl, 3-methyl-1,3-pentadienediyl, 1,4-ditolyl-1,3-butadienediyl and 1,4-bis(trimethylsilyl)-1,3-butadienediyl are particularly preferred. Other examples of dianions are those with heteroatoms, for instance of the structure

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the bridge being as defined. Additionally, weakly coordinating or non-coordinating anions of the type mentioned above are particularly preferred for charge compensation.

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Activation by means of such bulky anions is effected for example by reacting the D/A  $\pi$  complex compounds, especially the D/A metallocenes, with tris(pentafluorophenyl)borane, triphenylborane, triphenylaluminium, trityl tetrakis(pentafluorophenyl)borate or N,N-dialkylphenylammonium tetrakis(pentafluorophenyl)borate, as well as the corresponding alanes and alanates, or the corresponding phosphonium or sulfonium salts of borates or alanates, or alkali (alkaline earth) metal, thallium or silver salts of borates, alanates, carboranes, tosylates, triflates, perfluorocarboxylates, such as

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trifluoroacetate, or the corresponding acids. The D/A metallocenes used are preferably those whose anion equivalents X are alkyl, allyl, aryl or benzyl groups. Such derivatives can also be prepared "in situ" by first reacting D/A metallocenes which have other anion equivalents X, such as F, Cl, Br, OR etc., with alkylaluminium compounds, organolithium compounds, Grignard compounds or alkylzinc or alkyllead compounds. The resulting reaction products can be activated with above-mentioned boranes, borates, alanes or alanates without prior isolation.

Depending on the charge of M, the subscript n takes the value zero, one, two, three or four, preferably zero, one or two. Thus, depending inter alia on which subgroups they belong to, the above-mentioned subgroup metals can have valences/ charges of two to six, preferably two to four, two of which are compensated by the carbanions of the metallocene compound. Accordingly, the subscript n takes the value one in the case of  $\text{La}^{3+}$  and the value two in the case of  $\text{Zr}^{4+}$ ;  $n = \text{zero}$  for  $\text{Sm}^{2+}$ .

The metallocene compounds of formula (I) can be prepared by reacting either a compound of formula (II) above with a compound of formula (III) above, or a compound of formula (IV) above with a compound of formula (V) above, or a compound of formula (VI) above with a compound of formula (VII) above, or a compound of formula (VIII) above with a compound of formula (III) above, or a compound of formula (IV) above with a compound of formula (IX) above, or a compound of formula (X) above with a compound of formula (VII) above, with the elimination of alkali metal-X, alkaline earth metal- $\text{X}_2$ , silyl-X, germyl-X, stannyl-X or HX compounds, in an aprotic solvent, at temperatures of  $-78^\circ\text{C}$  to  $+120^\circ\text{C}$ , preferably of  $-40^\circ\text{C}$  to  $+70^\circ\text{C}$ , and in a molar ratio (II):(III), (IV):(V), (VI):(VII), (VIII):(III), (IV):(IX), or (X):(VII) of 1:0.5 - 2, preferably 1:0.8 - 1.2 and particularly preferably 1:1. In the case of reactions between (VIII) and (III), (IV) and (IX) or (X) and (VII), it is possible to dispense with an aprotic solvent if (VIII), (IX) or (X) is liquid under the reaction conditions. Examples of said eliminated compounds are:  $\text{TiCl}$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiF}$ ,  $\text{LiI}$ ,  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{KCl}$ ,  $\text{KF}$ ,  $\text{MgCl}_2$ ,  $\text{MgBr}_2$ ,  $\text{CaCl}_2$ ,  $\text{CaF}_2$ , trimethylchlorosilane, triethylchlorosilane, tri(n-butyl)chlorosilane, triphenylchlorosilane, trimethylchlorogermane, trimethylchlorostannane, dimethyl-amine, diethylamine.

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dibutylamine and other compounds which those skilled in the art can discern from the substitution pattern indicated above.

Compounds of formula (II) or (IV) thus represent carbanions with a cyclopentadienyl  
5 skeleton or a heterocyclic skeleton, which incorporate 1 to 3 donor groups used for D/A bridging, covalently bonded or as heterocyclic ring members, and contain a cation as the counterion for the negative charge of the cyclopentadienyl skeleton. Compounds of formula (VIII) are uncharged cyclic skeletons, also with 1 to 3 donor groups used for D/A bridging, but with readily cleavable leaving groups  $E(R^1R^2R^3)$ ,  
10 such as silyl, germyl or stannyl groups or hydrogen, in place of the ionic groups.

The second component for forming the metallocene compounds to be used according to the invention, namely the compound of formula (III) or (V), also represents a carbanion with a cyclopentadienyl skeleton which is identical to or different from the  
15 cyclopentadienyl skeleton of the compound (II) or (IV) but carries 1 to 3 acceptor groups in place of the donor groups. Analogously, compounds of formula (IX) are uncharged cyclopentadiene skeletons with 1 to 3 acceptor groups and also readily cleavable leaving groups  $F(R^4R^5R^6)$ .

20 By complete analogy, compounds of formula (VI) or (X) are starting materials with a preformed  $D \rightarrow A$  bond, which represent carbanion-counter cation compounds or uncharged cyclopentadiene skeletons with a possible total of 1 to 3  $D \rightarrow A$  bonds and give the metallocene compounds (I) by reaction with compounds of formula (VII).

25 Both the starting materials in the preparative process, i.e. (II) and (III), (IV) and (V), (VI) and (VII), (VIII) and (III), (IV) and (IX) or (X) and (VII), react spontaneously when brought together, with the simultaneous formation of the donor-acceptor group  $-D \rightarrow A-$  or the complexation of the metal cation M, and with the elimination of  $M'X$ ,  $E(R^1R^2R^3)X$ ,  $F(R^4R^5R^6)X$  or  $HX$ . For the sake of clarity, the substituents on D and A  
30 have been omitted in the representation of the donor-acceptor group.

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M' is one cation equivalent of an alkali (alkaline earth) metal, such as Li, Na, K,  $\frac{1}{2}$ Mg,  $\frac{1}{2}$ Ca,  $\frac{1}{2}$ Sr or  $\frac{1}{2}$ Ba, or thallium.

5 The compounds of formula (XIIIa + b) are prepared analogously in the manner indicated above.

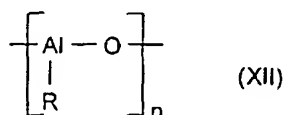
Solvents for the preparative process are polar or non-polar aprotic solvents such as aliphatic and aromatic hydrocarbons or aliphatic and aromatic halogenohydrocarbons. In principle, other aprotic solvents, such as those known to those skilled in the art, can  
10 also be used, although those with excessively high boiling points are less preferable in terms of the ease of working-up. Typical examples are: n-hexane, cyclohexane, pentane, heptane, petroleum ether, toluene, benzene, chlorobenzene, methylene chloride, diethyl ether, tetrahydrofuran and ethylene glycol dimethyl ether.

15 The starting materials of formulae (II), (III), (IV) and (V) can be prepared by processes known in the literature or by analogous processes. Thus, for example, analogously to J. of Organometallic Chem. (1971), 29, 227, the commercially available trimethylsilylcyclopentadiene can be reacted first with butyllithium and then with trimethylsilyl chloride to give bis(trimethylsilyl)cyclopentadiene. This in turn can be  
20 reacted with boron trichloride to give trimethylsilylcyclopentadienyldichloroborane (analogously to J. of Organometallic Chem. (1979), 169, 327), which can finally be reacted with titanium tetrachloride to give dichloro-borylcyclopentadienyltitanium trichloride analogously to J. of Organometallic Chem. (1979), 169, 373. This last-mentioned compound is already a prototype of the compounds of formula (III) and can  
25 be further reacted selectively with trimethylaluminium, the two chlorine atoms bonded to the boron atom being exchanged for methyl groups to give another compound of formula (III). Analogously to the descriptions of processes in J. Am. Chem. Soc. (1983), 105, 3882 and Organometallics (1982), 1, 1591, the commercially available cyclopentadienylthallium can be reacted with chlorodiphenylphosphine and further  
30 with butyllithium to give a prototype of compounds of formula (II). Another example which may be mentioned is the formation of dimethylstannyl-diphenylphosphinoindene by reacting indene first with butyllithium, as already

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mentioned above, and then with chlorodiphenylphosphine; further reaction, first with butyllithium again and then with chlorotributyltin, gives the target compound, which, after further reaction with zirconium tetrachloride, gives diphenyl-phosphinoindenyl-zirconium trichloride as a representative of compounds of formula (IV). Such

- 5 syntheses and preparative procedures are familiar to those skilled in the art who work in the field of metal-organic and element-organic chemistry, and are published in numerous literature references, only a few of which have been cited above as examples.
- 10 The examples listed below show how such heterocyclic precursors or catalysts according to the invention are obtainable. Thus pyrrolyllithium (formula II) can be prepared from pyrrole by reaction with butyllithium, for instance as described in J. Amer. Chem. Soc. (1982), 104, 2031. Trimethylstannylphosphole (formula VIII) is obtained by reacting 1-phenylphosphole with lithium and then with aluminium
- 15 trichloride to give phospholylithium (formula II), which in turn reacts further with trimethylchlorostannane to give trimethylstannylphosphole; cf.: J. Chem. Soc. Chem. Comm. (1988), 770. This compound can be reacted with titanium tetrachloride to give phospholyltitanium trichloride (formula IV).
- 20  $10^1$  to  $10^{12}$  mol of comonomers are reacted per mol of  $\pi$  complex compounds or metallocene compounds. The  $\pi$  complex compounds or metallocene compounds can be used together with cocatalysts. The relative proportions of metallocene compound or  $\pi$  complex compound and cocatalyst are 1 to 100,000 mol of cocatalyst per mol of metallocene or  $\pi$  complex compound. Aluminoxane compounds are examples of
- 25 cocatalysts. These are understood as meaning compounds of the formula



- 30 in which

R is  $\text{C}_1$ - $\text{C}_{20}$ -alkyl,  $\text{C}_6$ - $\text{C}_{12}$ -aryl or benzyl and

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n is a number from 2 to 50, preferably 10 to 35.

It is also possible to use a mixture of different aluminoxanes or a mixture of their precursors (alkylaluminium compounds) in combination with water (in gaseous, liquid, solid or bound form, for instance as water of crystallization). The water can also be introduced as (residual) moisture in the polymerization medium, the monomer or a support like silica gel. The boron compounds analogous to formula (XII) are suitable as well.

The bonds projecting from the square brackets of formula (XII) carry R groups or  $AlR_2$  groups as end groups of the oligomeric aluminoxane. Such aluminoxanes are normally present as a mixture of several with different chain lengths. Detailed study has also revealed aluminoxanes of cyclic or cage-like structure. Aluminoxanes are commercially available compounds. In the special case where  $R = CH_3$ , they are referred to as methylaluminoxanes (MAO).

Other cocatalysts are alkylaluminium compounds, alkyl lithium compounds, organo-magnesium compounds such as Grignard compounds, or partially hydrolyzed organo-boron compounds. The preferred cocatalysts are aluminoxanes.

The activation with the cocatalyst or the production of the bulky non-coordinating or weakly coordinating anion can be carried out in an autoclave or in a separate reaction vessel (preformation). The activation can be effected in the presence or absence of the monomer(s) to be polymerized. The activation can be carried out in an aliphatic, aromatic or halogenated solvent or suspending agent.

The  $\pi$  complex compounds or metallocene compounds and the aluminoxanes can be used either as such in homogeneous form or individually or together in heterogeneous form on supports. Said support can be of an inorganic or organic nature, such as silica gel,  $Al_2O_3$ ,  $B_2O_3$ ,  $MgCl_2$ , NaCl, polysiloxanes, cellulose derivatives, starch derivatives and other polymers. It is possible here either to apply the  $\pi$  complex compound or

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metallocene compound first or to apply the aluminoxane first to the support and then to add the other component. By the same token, however, it is also possible to activate the  $\pi$  complex compound or metallocene compound in homogeneous or heterogeneous form with the aluminoxane and then to apply the activated metallocene compound to the support.

The supports are preferably thermally and/or chemically pretreated in order to adjust the water content or the OH group concentration to a defined value or keep it as low as possible. A chemical pretreatment can consist e.g. in the reaction of the support with alkylaluminium compound. Inorganic supports are usually heated at 100°C to 1000°C for 1 to 100 hours before use. The surface area of such inorganic supports, especially of silica (SiO<sub>2</sub>), is between 10 and 1000 m<sup>2</sup>/g, preferably between 100 and 800 m<sup>2</sup>/g. The particle diameter is between 0.1 and 500 micrometres ( $\mu$ ), preferably between 10 and 200  $\mu$ .

Examples of olefins and diolefins to be reacted by (co)polymerization are ethylene, propylene, but-1-ene, pent-1-ene, hex-1-ene, oct-1-ene, 3-methylbut-1-ene, 4-methylpent-1-ene, 4-methylhex-1-ene, 1,4-hexadiene, 1,5-hexadiene, 1,6-octadiene, 1,7-octadiene, branched non-conjugated dienes and other olefins and diolefins known to those skilled in the art. Such olefins and diolefins can also be substituted, for example with phenyl or substituted phenyl; examples of compounds of this type are styrene, vinylsilane and trimethylallylsilane. Preferred monomers are: ethylene, propylene, butene, hexene, octene, 1,4-hexadiene, 1,6-octadiene, 1,7-octadiene and methyl-substituted octadienes with a terminal double bond, for instance 7-methyl-1,6-octadiene.

In principle,  $\alpha$ -olefins having up to 20 C atoms can also be used. In cases where  $\alpha$ -olefins having 2 to 4 C atoms are used in combination with higher  $\alpha$ -olefins, dienes or other comonomers, the C<sub>2</sub>-C<sub>4</sub>- $\alpha$ -olefins are present in a proportion of 25 to 95 wt.%, preferably 30 to 80 wt.%, based on the total weight. On the other hand, 1-octene, for instance, is present in an amount of 5 to 35 wt.%, preferably 7.5 to 25 wt.%. 0.1 to 20 wt.% of one or more of said diolefins is also present.



- 30 -

Apart from the stated dienes, the following open-chain, monocyclic and polycyclic dienes may also be mentioned: 5-methyl-1,4-hexadiene, 3,7-dimethyl-1,6-octadiene, cyclopentadiene, 1,4-hexadiene, 1,5-cyclooctadiene, tetrahydroindene, methyltetra-  
5 hydroindene, dicyclopentadiene, bicyclo(2.2.1)-2,5-heptadiene, norbornenes with substituents such as alkenyl, alkylidene, cycloalkenyl or cycloalkylidene, for instance 5-methylene-2-norbornene (MNB), 5-ethylidene-2-norbornene, 5-isopropylidene-2-norbornene and 5-vinyl-2-norbornene. allylcyclohexene and vinylcyclohexene.

10 Other preferred monomers in addition to those mentioned above are: dicyclopentadiene, 1,4-hexadiene, 5-methyl-2-norbornene, 5-ethylidene-2-norbornene and 5-vinyl-2-norbornene. Of course it is also possible to use mixtures of several of these.

The process according to the invention is carried out in the bulk, solution, high-  
15 temperature solution, slurry or gas phase, depending on whether a soluble or insoluble catalyst of the type described above is used. The solution phase or the slurry phase can be formed of the comonomers alone, i.e. without using an additional solvent. In the case where a solvent is used, inert solvents are suitable for the purpose, examples being aliphatic or cycloaliphatic hydrocarbons such as propane, butane, pentane,  
20 hexane, cyclohexane and propene (which is a (co)monomer at the same time), petroleum naphtha fractions or diesel oil fractions (optionally after hydrogenation), toluene, chlorobenzene, o-dichlorobenzene or chloronaphthalene. In the case of low-boiling solvents, the liquid phase can be maintained by the application of a sufficient reaction pressure; such interrelations are known to those skilled in the art. According  
25 to the invention, the process is carried out in one or more reactors or reaction zones, e.g. in reactor cascades, it being possible to employ different polymerization conditions.

The above-mentioned temperatures and pressures are employed. The temperatures  
30 applied are in the range from about 0 to 150°C for the bulk, solution and slurry procedures, 40 to 200° for the high-temperature liquid procedure and about 20 to 100°C for the gas phase. For economic reasons, the pressures frequently do not exceed

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a value of 30 bar, preferably 20 bar. According to the invention, the process is carried out in one or more reactors or reaction zones, e.g. in a reactor cascade; if several reactors are used, it is possible to employ different polymerization conditions.

- 5 Examples of elastomers which can be prepared according to the invention are those of the following types: ethylene/propylene copolymer (EPM), ethylene/butene copolymer (EBM), ethylene/pentene copolymer, ethylene/hexene copolymer (EHM), ethylene/heptene copolymer, ethylene/octene copolymer (EOM) and ethylene/propylene/butene copolymer which do not contain crosslinking monomers, and  
10 ethylene/propylene/diene copolymer (EPDM), ethylene/butene/diene copolymer (EBDM) and ethylene/hexene(or octene)/diene copolymer (EHDM or EODM) which do contain crosslinking monomers such as ethyldenenorbornene: the proportion of crosslinking monomers, e.g. diene, is up to 20 wt.% of all the comonomers, e.g. 0.1 to 20 wt.%, preferably 1 to 12 wt.% and particularly preferably 2 to 8 wt.%. Preferred  
15 elastomers are those of the EPM and EPDM type.

Such elastomers are distinguished by a good elasticity, even at low temperatures, and by at least a partially amorphous structure (moderate or low crystallinity, i.e. a degree of crystallinity of less than 30%, preferably less than 20% and particularly preferably  
20 less than 10%, measured by methods known to those skilled in the art, especially DSC) with a low glass transition temperature  $T_g$ .  $T_g$  is preferably below  $-20^{\circ}\text{C}$ , particularly preferably below  $-40^{\circ}\text{C}$ . Said elastomers have molecular weights  $M_w$  greater than 10 kg/mol, preferably greater than 100 kg/mol and particularly preferably greater than 200 kg/mol. It is possible to reach  $M_w$  values of up to 10,000 kg/mol and especially of up  
25 to 5,000 kg/mol. According to the invention, it is particularly possible to reach said high molecular weights and to achieve a uniform distribution of the comonomers. In the case of dienes or other crosslinkable comonomers, the uniform distribution allows a high degree of crosslinking during vulcanization. It is also possible to obtain products with long branched chains. All the elastomers which can be prepared  
30 according to the invention are characterized in particular by one or more melting peaks. At least one of these melting peaks has its maximum at a melting temperature  $T_m$  above  $+40^{\circ}\text{C}$ , preferably above  $+50^{\circ}\text{C}$  and particularly preferably above  $60^{\circ}\text{C}$ .

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Such melting peaks are further characterized by their half-intensity width. Preferably, at least one of the melting peaks has a half-intensity width of at most 30°C. The elastomers which can be prepared according to the invention exhibit an improved green strength.

5

Through the donor-acceptor bridge, the  $\pi$  complex compounds to be used according to the invention, especially the metallocene compounds, allow a definite opening of the two cyclopentadienyl skeletons in the manner of a beak, thereby ensuring not only a high activity but also a controlled selectivity, a controlled molecular weight  
10 distribution and a uniform incorporation of (co)monomers. As a result of a definite beak-like opening, there is also room for bulky (co)monomers. A high uniformity of the molecular weight distribution is also a consequence of the uniform and definite site of the polymerization effected by insertion (single site catalyst).

15 The molecular weight distribution can be specifically changed (broadened) by the simultaneous use of several D/A catalysts in order to produce a particular profile of material properties. Accordingly, it is also possible to use one or more D/A catalysts in combination with other metallocenes which do not have D/A bridges.

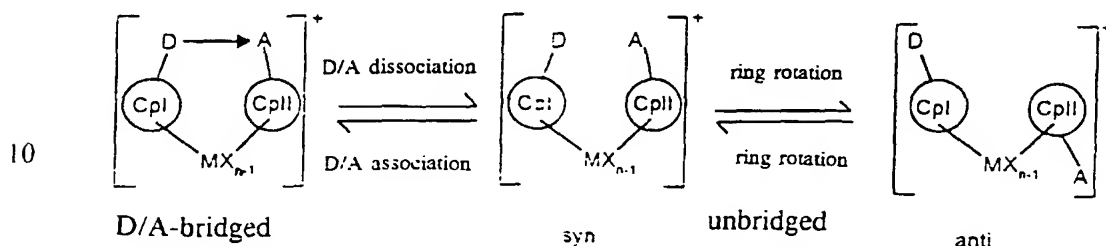
20 The D/A structure can provide an extra stabilization of the catalysts right up to high temperatures, so the catalysts can also be employed in the high temperature range from 80 to 250°C, preferably 80 to 200°C. The possible thermal dissociation of the donor-acceptor bond is reversible and, through this self organization process and self repair mechanism, results in particularly high-quality catalyst properties.

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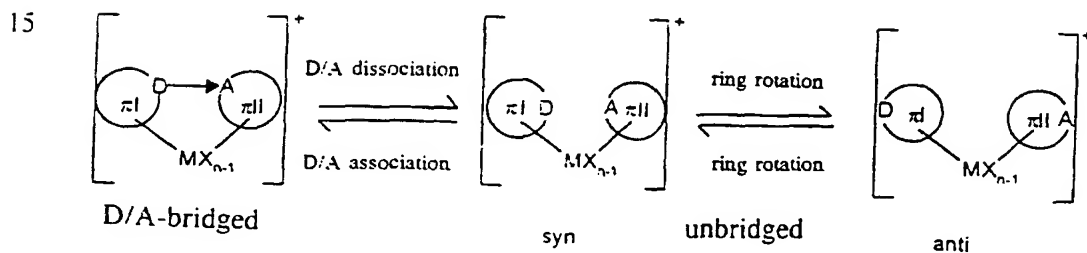
It has also been observed that the copolymerization behaviour of the metallocene compounds to be used according to the invention varies with temperature. This phenomenon has not yet been fully studied, but it could be consistent with the observation that coordinate bonds which are superimposed by an ionic bond, like the  
30 donor-acceptor bonds in the metallocene compounds according to the invention, exhibit an increasing reversibility at higher temperature. Thus, for example, it has been observed in the copolymerization of ethylene and propylene that, with the same

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initial amount of both comonomers, a copolymer with a high propylene content is formed at low copolymerization temperature, whereas the propylene content drops with increasing polymerization temperature until ultimately polymers containing predominantly ethylene are formed at high temperature. The reversible dissociation and association of the D/A structure and the relative rotation of the Cp skeletons which this allows can be represented schematically as follows:



or



Another valuable property of the D/A  $\pi$  complex compounds according to the invention, especially the D/A metallocene compounds, is the possibility of self activation and hence of doing without expensive catalysts, especially in the case of dianionic x x- derivatives.

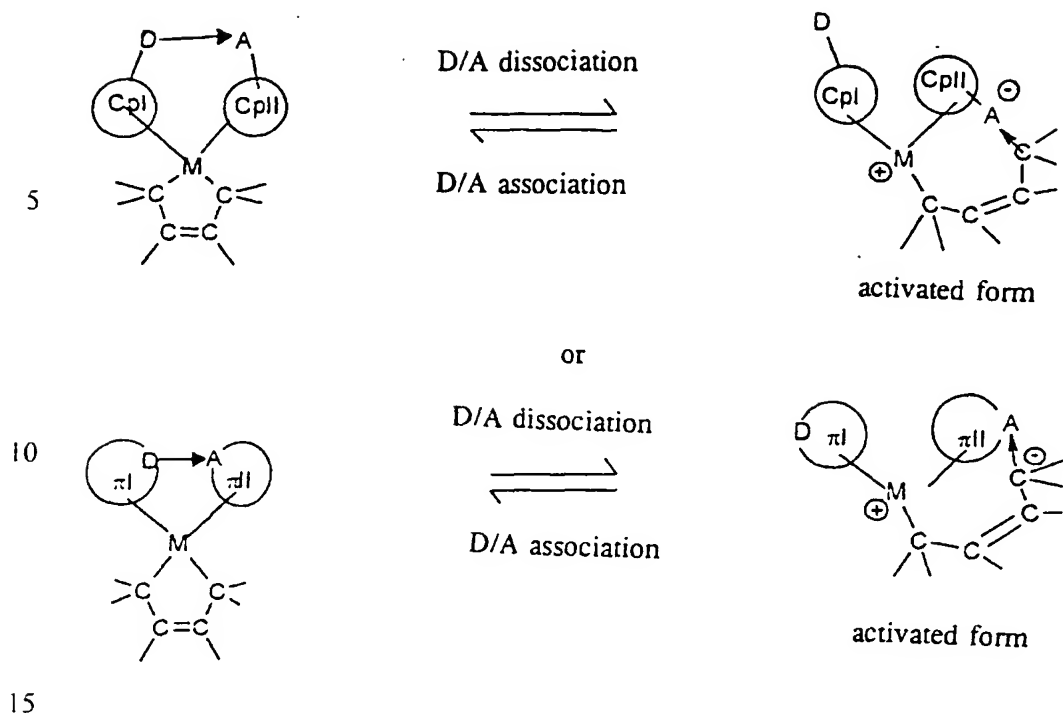
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Here, in the open form of the D/A  $\pi$  complex compounds, for example D/A metallocene compound, the acceptor atom A binds an X ligand, for example one side of a dianion, to form a zwitterionic metallocene structure, thereby producing a positive charge on the transition metal, while the acceptor atom A takes on a negative charge.

30

Said self activation can take place intramolecularly or intermolecularly. The intramolecular mechanism may be exemplified by the preferred linking of two X ligands to one chelate ligand, i.e. of the butadienediyl derivative:

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The binding site between the transition metal M and H or substituted or unsubstituted C (in the formal example, substituted C of the butadienediyl dianion shown) is then the site of olefin insertion for polymerization.

20

Figures 1a-e show examples of DSC measurements of the 2nd heating on EPDM samples of the present invention. Fig. 1a represents an amorphous type of EPDM with a small melting peak above 50°C and an enthalpy of fusion of only 2 - 3 J/g, corresponding to a crystallinity of  $\leq 1\%$ . Fig. 1b shows a partially crystalline type with a pronounced melting peak above 90°C and an enthalpy of fusion of ca. 29 J/g,

25

corresponding to a crystallinity of ca. 10%.

Fig. 1c depicts a partially crystalline type with low-temperature crystallinity ( $T_{m1} = -10^\circ\text{C}$ ,  $\Delta H_m = 15 \text{ J/g}$ ) and a discrete melting peak  $T_{m2}$  according to the invention at 126°C. Fig. 1d shows a partially crystalline material with a low glass transition temperature  $T_g$  of  $-54^\circ\text{C}$  and a discrete melting peak at 100°C, which corresponds to a

30

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crystallinity of about 3% ( $\Delta H_m = 8 \text{ J/g}$ ). Fig. 1e shows a rubber with a  $T_g$  of  $-52^\circ\text{C}$ , a high-temperature crystallinity of ca. 4% and a  $T_m$  of  $112^\circ\text{C}$ .

Figure 1f relates to the EPDM of Example 7.

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**Examples**

All the reactions were carried out under strictly anaerobic conditions using Schlenk techniques or the high-vacuum technique. The solvents used were dry and saturated with argon. Chemical shifts  $\delta$  are given in ppm relative to the appropriate standard:  $^1\text{H}$  (tetramethylsilane),  $^{13}\text{C}$  (tetramethylsilane),  $^{31}\text{P}$  (85%  $\text{H}_3\text{PO}_4$ ),  $^{11}\text{B}$  (boron trifluoride etherate,  $\delta = -18.1$  ppm). Minus signs signify a shift to higher field.

**Example 1** (Bis(trimethylsilyl)cyclopentadiene, compound 1)

10

14.7 g (0.106 mol) of trimethylsilylcyclopentadiene (obtained from Fluka) and 150 ml of tetrahydrofuran (THF) were placed in a reaction flask and cooled to  $0^\circ\text{C}$ . 47.4 ml of a solution of butyllithium in n-hexane (2.3 molar; total amount 0.109 mol) were added dropwise over 20 minutes. When the addition was complete, the yellow solution was stirred for a further one hour and the cooling bath was then removed. At room temperature the solution was stirred for a further one hour and then cooled to  $-20^\circ\text{C}$ . 14.8 ml (0.117 mol) of trimethylsilyl chloride were then added dropwise over 10 minutes and the reaction mixture was stirred for two hours at  $-10^\circ\text{C}$ . The cooling bath was then removed and the reaction solution was heated to room temperature and subsequently stirred for a further one hour. The reaction mixture was filtered through Célite: the filter was washed with hexane and the hexane was removed from the combined filtrates under vacuum. On distillation at  $26^\circ\text{C}$  under 0.4 mbar, the crude product gave 19 g of pure compound 1 (85% of the theoretical yield). Boiling point and NMR data are consistent with the literature (J. Organometallic Chem. **29**, (1971), 227; *ibid.* **30**, (1971), C 57; J. Am. Chem. Soc. **102**, (1980), 4429; J. Gen. Chem. USSR, Eng. Transl. **43**, (1973), 1970; J. Chem. Soc., Dalton Trans. **1980**, 1156).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 6.74$  (m, 2H), 6.43 (m, 2H), -0.04 (s, 18H).

25

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**Example 2** (Trimethylsilylcyclopentadienyldichloroborane, compound 2)

30

16 g (0.076 mol) of compound 1 were placed in a round-bottomed flask equipped with a dry ice cooling bath. 8.9 g (0.076 mol) of  $\text{BCl}_3$  were condensed into a Schlenk tube

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at -78°C and then added dropwise to the flask over a period of 5 minutes. The reaction mixture was slowly heated to room temperature over 1 hour and then kept at 55 to 60°C for a further 2 hours. All the volatile compounds were removed under vacuum (3 mm Hg = 4 mbar). Subsequent distillation at 39°C and 0.012 mbar gave 14.1 g of compound 2 (85% of the theoretical yield). The <sup>1</sup>H NMR data are consistent with the literature and showed that a number of isomers had been prepared (cf. J. Organometallic Chem. **169**, (1979), 327).

<sup>11</sup>B NMR (64.2 MHz, C<sub>6</sub>D<sub>6</sub>): δ = +31.5.

10 **Example 3** (Tributylstannyldiphenylphosphinoindene, compound 3)

10 g (0.086 mol) of indene were placed in a round-bottomed flask, diluted with 200 ml of diethyl ether and cooled to -20°C. 36 ml of a 2.36 molar solution of butyllithium (0.085 mol) in n-hexane were added to this solution, which immediately assumed a yellow colouration. The cooling bath was removed and the reaction mixture was allowed to warm up to room temperature and stirred for a further one hour. The reaction mixture was then cooled to 0°C again and 19 g (15.9 ml, 0.086 mol) of diphenylchlorophosphine were added to form a precipitate. The cooling bath was removed again and the solution was able to warm up to room temperature, stirring being continued for a further one hour. The solution was then cooled to -20°C again and 36 ml (0.085 mol) of butyllithium in n-hexane were added dropwise. When the addition was complete, the cooling bath was removed again and the temperature rose to room temperature; the solution was stirred for a further 1.5 hours. The suspension was then cooled to 0°C again and 28 g (0.086 mol) of tributyltin chloride were added dropwise. The resulting suspension was heated to room temperature and stirred for a further 1.5 hours; it was then filtered through a frit and the solvent was removed under vacuum to leave 46.9 g of compound 3 (92% of the theoretical yield) in the form of a heavy yellow oil.

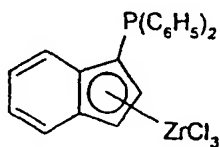
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.5 - 7.3 (m, 6H), 7.28 (bs, 6H), 7.14 (pseudo dt, 7.3 Hz/1.0 Hz, 1H), 7.08 (t, J = 7.3 Hz, 1H), 6.5 (bm, 1H), 4.24 (bs, 1H), 1.4 - 1.25 (m, 6H), 1.25 - 1.15 (m, 6H), 0.82 (t, J = 7.2 Hz, 9H), 0.53 (t, J = 8 Hz, 6H); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>): δ = -20.6.



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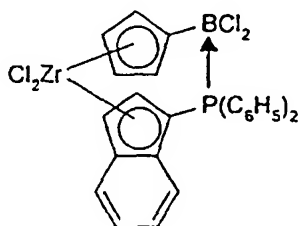
**Example 4** (Diphenylphosphinoindenylzirconium trichloride, compound 4)

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A solution of 37 g (0.0628 mol) of compound 3 in 300 ml of toluene was added over 3 hours to a suspension of 14.6 g of  $ZrCl_4$  (99.9% pure, 0.0628 mol, obtained from Aldrich) in 100 ml of toluene at room temperature. The solution immediately became red and slowly turned orange and ultimately yellow. After stirring for 4 hours, the yellow precipitate was filtered off and washed with toluene and then with hexane. The solid was dried under vacuum to give 15.3 g (50% of the theoretical yield) of compound 4 in the form of a free-flowing yellow powder. The yield could easily be increased to over 70% by working at a lower temperature, e.g. 30 min at  $-30^\circ C$  and 5 hours at  $0^\circ C$ . The product could be purified further by washing out residual tin compound using pentane in a Soxhlet extractor (extraction time: 8 hours).

20

**Example 5** ( $((C_6H_5)_2P-BCl_2$ -bridged indenylcyclopentadienylzirconium dichloride, compound 5)

25

5

4.43 g (0.0089 mol) of purified compound 4 and 100 ml of toluene were placed in a Schlenk tube. 1.95 g (0.0089 mol) of compound 2 were added to this suspension. The yellow suspension was stirred at room temperature for 6 hours, during which time a whitish precipitate was formed. This precipitate (4.1 g, 75% of the theoretical yield) was recovered by filtration and found to be an essentially pure material.

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$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 7.86 (pseudo ddd,  $J$  = 8.5/2.5/1 Hz, 1H), 7.75 - 7.55 (m, 10H), 7.35 (pseudo ddd,  $J$  = 8.5/6.9/0.9 Hz, 1H), 7.32 (bt,  $J$  = 3.1 Hz, 1H), 7.22 (pseudo ddd,  $J$  = 8.8/6.8/1.1 Hz, 1H), 7.06 (pseudo ddd,  $J$  = 3.4/3.4/0.8 Hz, 1H), 6.92 (m, 1H), 6.72 (m, 1H), 6.70 (bm, 1H), 6.61 (pseudo q,  $J$  = 2.3 Hz, 1H), 6.53 (bd, 8.7 Hz, 1H);  $^{31}\text{P}$  NMR (161.9 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 6.2 (bm);  $^{11}\text{B}$  NMR (64.2 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = -18 (b).

**Example 6** (Catalyst alkylation)

11 mg (corresponding to  $18 \cdot 10^{-6}$  mol) of the donor-acceptor metallocene **5** were weighed into a dry Schlenk vessel under argon, dissolved in 1.8 ml of toluene containing 1.8 mmol of triisobutylaluminium (TIBA) and stirred at room temperature for 30 minutes. The yellowish brown solution was then diluted with 10 ml of toluene containing 0.05 mmol of TIBA. An aliquot of this solution, i.e. 0.65 ml, was used for the polymerization.

**Example 7** (EPDM synthesis)

100 ml of dry toluene distilled under inert gas, 1 g of ethylenenorbornene (ENB) distilled over sodium, 0.1 mmol of TIBA and 10 g of propene were placed in a dry, oxygen-free 300 ml V4A steel autoclave and heated to 80°C, with magnetic stirring. The resulting internal pressure of ca. 7 bar was increased by 2 bar to 9 bar with ethene. By means of a pressure lock,  $1 \cdot 10^{-6}$  mol of the alkylated D/A metallocene **5** in 0.65 ml of the solution of Example 6 was transferred to the autoclave and the polymerization was then started immediately by the addition, via the pressure lock, of  $4 \cdot 10^{-6}$  mol (3.2 mg) of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate in 3.7 ml of argon-saturated chlorobenzene which had been distilled over calcium hydride.

The internal temperature rose to 82°C. After 30 minutes of polymerization, the reaction was stopped by the addition of ethanol and the polymer was precipitated in 500 ml of ethanol/concentrated hydrochloric acid (90/10), stirred for 1 hour and then

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filtered off, washed with ethanol and dried to constant weight at 90°C in a vacuum drying cabinet.

EPDM yield: 3.6 g

5 Catalyst activity: 7.2 t of EPDM per mol of catalyst per hour

Intrinsic viscosity (ortho-  
dichlorobenzene, 140°C): 1.08 dl/g

Chemical composition according to FT-IR analysis:

10 64 wt.% of ethene  
32 wt.% of propene  
4 wt.% of ENB

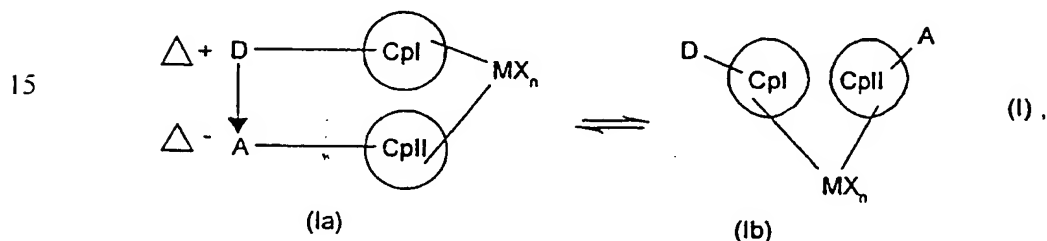
DSC (2nd heating): transition temperature  $T_c = -53^\circ\text{C}$   
glass transition temperature  $T_g = -47^\circ\text{C}$   
melting temperature  $T_{m1} = +18^\circ\text{C}$   
15  $T_{m2} = +111^\circ\text{C}$

Width-at-half-height (half-intensity width) of the 2nd melting peak: 11°C

Enthalpy of fusion  $\Delta H_m = 38 \text{ J/g}$

**Claims**

1. Process for the preparation of saturated or unsaturated elastomers which, in addition to the amorphous structure and a low glass transition temperature  $T_g$  in the DSC measurement, have one or more melting peaks, at least one of which has its maximum at a melting temperature ( $T_m$ ) above  $+40^\circ\text{C}$ , by the (co)polymerization of monomers selected from the group consisting of  $\text{C}_2\text{-C}_8$ - $\alpha$ -olefins, open-chain monocyclic and/or polycyclic  $\text{C}_4\text{-C}_{15}$ -diolefins and styrene, in the bulk, solution, high-temperature solution, slurry or gas phase, in the presence of metal-organic catalysts which can be activated by cocatalysts, which process is characterized in that the metal-organic catalysts used are metallocene compounds of the formula



20 in which

CpI and CpII are two identical or different carbanions with a cyclopentadienyl-containing structure, in which one H atom to all the H atoms can be substituted by identical or different radicals selected from the group consisting of linear or branched  $\text{C}_1\text{-C}_{20}$ -alkyl which can be monosubstituted to fully substituted by halogen, monosubstituted to trisubstituted by phenyl and monosubstituted to trisubstituted by vinyl,  $\text{C}_6\text{-C}_{12}$ -aryl, halogenoaryl having 6 to 12 C atoms, and organometallic substituents such as silyl, trimethylsilyl or ferrocenyl, and can be monosubstituted or disubstituted by D and A.

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D is a donor atom which can additionally carry substituents and which, in its particular bonding state, possesses at least one free electron pair,

5 A is an acceptor atom which can additionally carry substituents and which, in its particular bonding state, has an electron pair gap,

10 D and A being linked by a reversible coordinate bond in such a way that the donor group takes on a (partial) positive charge and the acceptor group a (partial) negative charge,

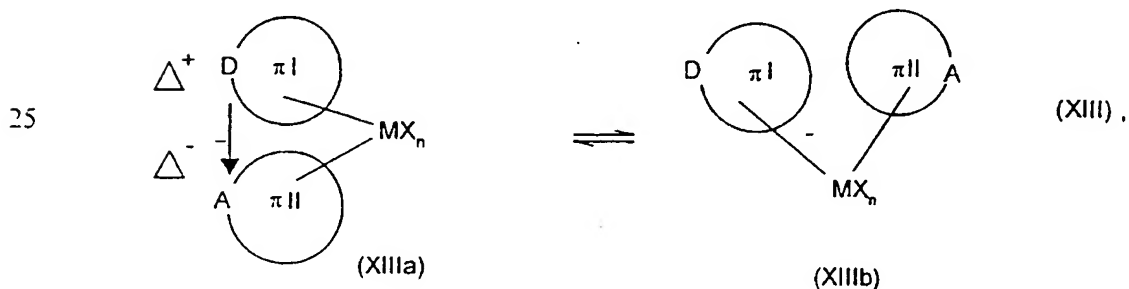
M is a transition metal of subgroup III, IV, V or VI of the periodic table of the elements (Mendeleeff), including the lanthanides and actinides.

15 X is one anion equivalent and

n is the number zero, one, two, three or four, depending on the charge of M,

or

20  $\pi$  complex compounds and especially metallocene compounds of the formula



30

in which

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$\pi I$  and  $\pi II$  are different charged or electrically neutral  $\pi$  systems which can be fused with one or two unsaturated or saturated five-membered or six-membered rings,

5 D is a donor atom which is a substituent of  $\pi I$  or part of the  $\pi$  system of  $\pi I$  and which, in its particular bonding state, possesses at least one free electron pair,

10 A is an acceptor atom which is a substituent of  $\pi II$  or part of the  $\pi$  system of  $\pi II$  and which, in its particular bonding state, has an electron pair gap,

15 D and A being linked by a reversible coordinate bond in such a way that the donor group takes on a (partial) positive charge and the acceptor group a (partial) negative charge, and at least one of D and A being part of its corresponding  $\pi$  system,

it being possible for D and A in turn to carry substituents,

20 it being possible for each  $\pi$  system or each fused ring system to contain one or more D or A, or D and A, and

25 it being possible, in  $\pi I$  and  $\pi II$  in the non-fused or in the fused form, for one H atom to all the H atoms of the  $\pi$  system to be substituted independently of one another by identical or different radicals selected from the group consisting of linear or branched  $C_1$ - $C_{20}$ -alkyl which can be mono-substituted to fully substituted by halogen, monosubstituted to trisubstituted by phenyl and monosubstituted to trisubstituted by vinyl,  $C_6$ - $C_{12}$ -aryl, halogenoaryl having 6 to 12 C atoms, and organometallic substituents such as silyl, trimethylsilyl and ferrocenyl, and to be monosubstituted or disubstituted by D and A, so that the reversible coordinate  $D \rightarrow A$  bond is formed (i) between D and A where they  
30 are both parts of the particular  $\pi$  system or the fused ring system, or (ii)

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between D and A where D or A is part of the  $\pi$  system and the other one is a substituent of the non-fused  $\pi$  system or the fused ring system, or (iii) between D and A where both D and A are such substituents, wherein, in the case of (iii), at least one additional D or A, or both, are part of the  $\pi$  system or the fused ring system.

M and X are as defined above and

n is the number zero, one, two, three or four, depending on the charges of M and those of  $\pi$ I and  $\pi$ II.

2. Process according to Claim 1, characterized in that the metallocene compounds or the  $\pi$  complex compounds are used as catalysts in an amount of  $10^1$  to  $10^{12}$  mol of monomers per mol of metallocene or  $\pi$  complex compound.
3. Process according to Claim 1, characterized in that, if present, the solvents used are selected from the group consisting of saturated and aromatic hydrocarbons or saturated or aromatic halogenohydrocarbons.
4. Process according to Claim 1, characterized in that, in the metallocene compounds, the carbanions CpI and CpII or the  $\pi$  system  $\pi$ I are a cyclopentadienyl skeleton selected from the group consisting of cyclopentadiene, substituted cyclopentadiene, indene, substituted indene, fluorene and substituted fluorene, in which 1 to 4 substituents selected from the group consisting of C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>1</sub>-C<sub>20</sub>-alkoxy, halogen, C<sub>6</sub>-C<sub>12</sub>-aryl, halogenophenyl, D and A are present per cyclopentadiene ring or fused benzene ring, D and A being as defined in Claim 1 and it being possible for fused aromatic rings to be partially or completely hydrogenated.
5. Process according to Claim 1, characterized in that, in the metallocene compounds, elements selected from the group consisting of N, P, As, Sb, Bi,

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O, S, Se, Te, F, Cl, Br and I, preferably N, P, O and S, are present as donor atoms D.

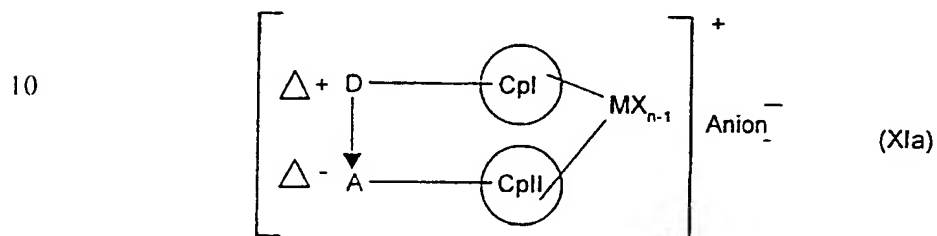
6. Process according to Claim 1, characterized in that, in the metallocene  
5 compounds, elements selected from the group consisting of B, Al, Ga, In and Tl, preferably B, Al and Ga, are present as acceptor atoms A.
7. Process according to Claim 1, characterized in that, in the metallocene  
10 compounds or  $\pi$  complex compounds, donor-acceptor bridges selected from the group consisting of  $N \rightarrow B$ ,  $N \rightarrow Al$ ,  $P \rightarrow B$ ,  $P \rightarrow Al$ ,  $O \rightarrow B$ ,  $O \rightarrow Al$ ,  $Cl \rightarrow B$ ,  $Cl \rightarrow Al$ ,  $C=O \rightarrow B$  and  $C=O \rightarrow Al$  are present.
8. Process according to Claim 1, characterized in that, in the metallocene  
15 compounds, M is Sc, Y, La, Sm, Nd, Lu, Ti, Zr, Hf, Th, V, Nb, Ta or Cr, preferably Ti, Zr, Hf, V, Nb or Ta.
9. Process according to Claim 1, characterized in that the metallocene compounds  
20 or the  $\pi$  complex compounds are used together with an aluminoxane, alane or alanate, a borane or borate and optionally other cocatalysts and/or metal alkyls as the catalyst system.
10. Process according to Claim 1, characterized in that rearrangement products of  
25 metallocene compounds or  $\pi$  complex compounds according to Claim 1 under self activation are used in which, after opening of the D/A bond, the acceptor atom A binds an X ligand to form a zwitterionic metallocene complex structure or  $\pi$  complex structure, a positive charge being produced on the transition metal M and a negative charge on the acceptor atom A, and another X ligand being H or substituted or unsubstituted C in whose bond to the transition metal M the olefin insertion for polymerization takes place, preferably 2 X ligands  
30 being linked to one chelate ligand.



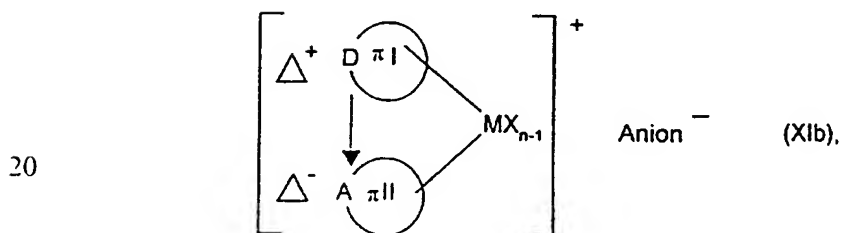
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11. Process according to Claim 1, characterized in that  $\pi$  complex compounds according to Claim 1 are used in which one of the atoms D or A, preferably D, is part of the ring of the corresponding  $\pi$  system.

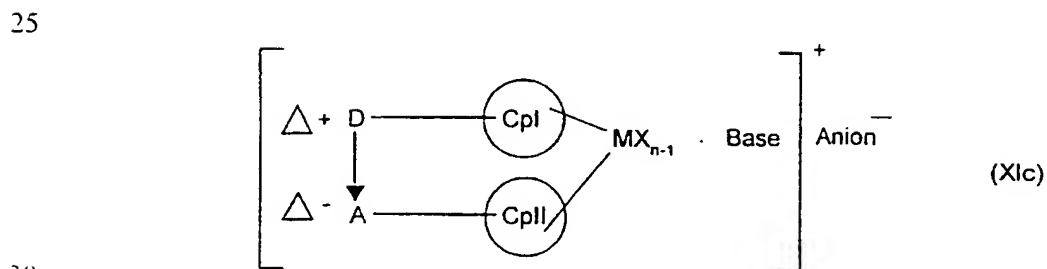
5 12. Process according to Claim 1, characterized in that reaction products of formula (XI) or (XIa) of ionizing agents with metallocene compounds or  $\pi$  complexes of formula (I) or (XIII):



15 or



or

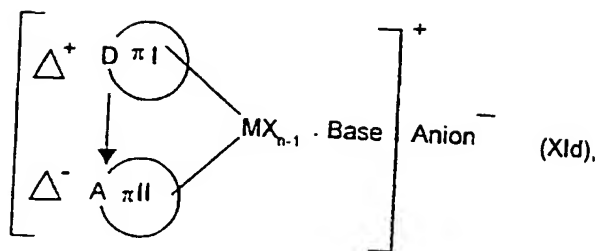


30

or

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5



in which

10      Anion represents the entire bulky, poorly coordinating anion and Base represents a Lewis base,

are used.

15      13.      Process according to Claim 1, characterized in that the metallocene compounds or  $\pi$  complex compounds are used on a support as heterogeneous catalysts.

14.      Process according to Claim 1, characterized in that it is aimed at the preparation of EPM and EPDM.

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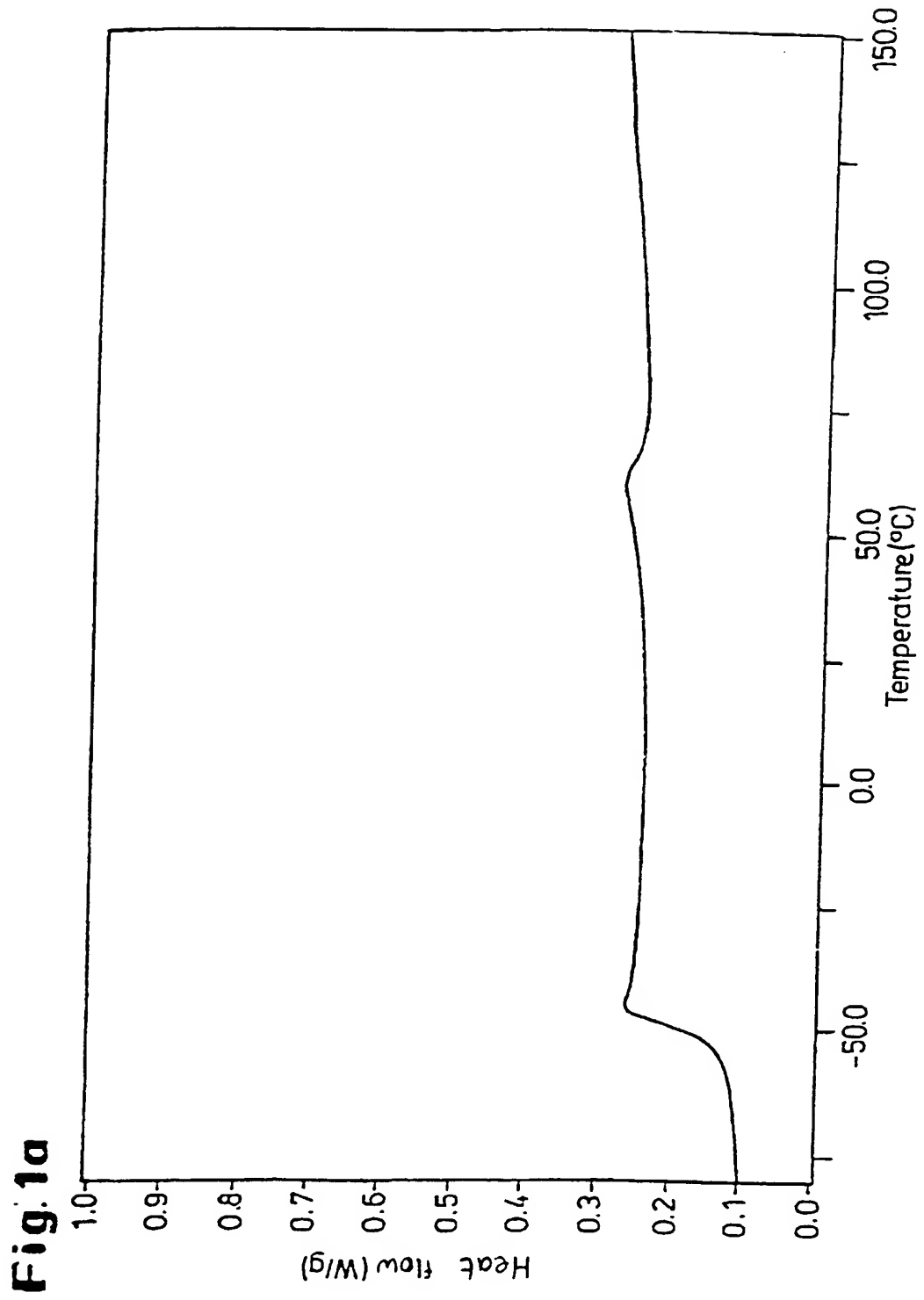
15.      Process according to Claim 1, characterized in that the melting temperature  $T_m$  of at least one melting peak is above +50°C.

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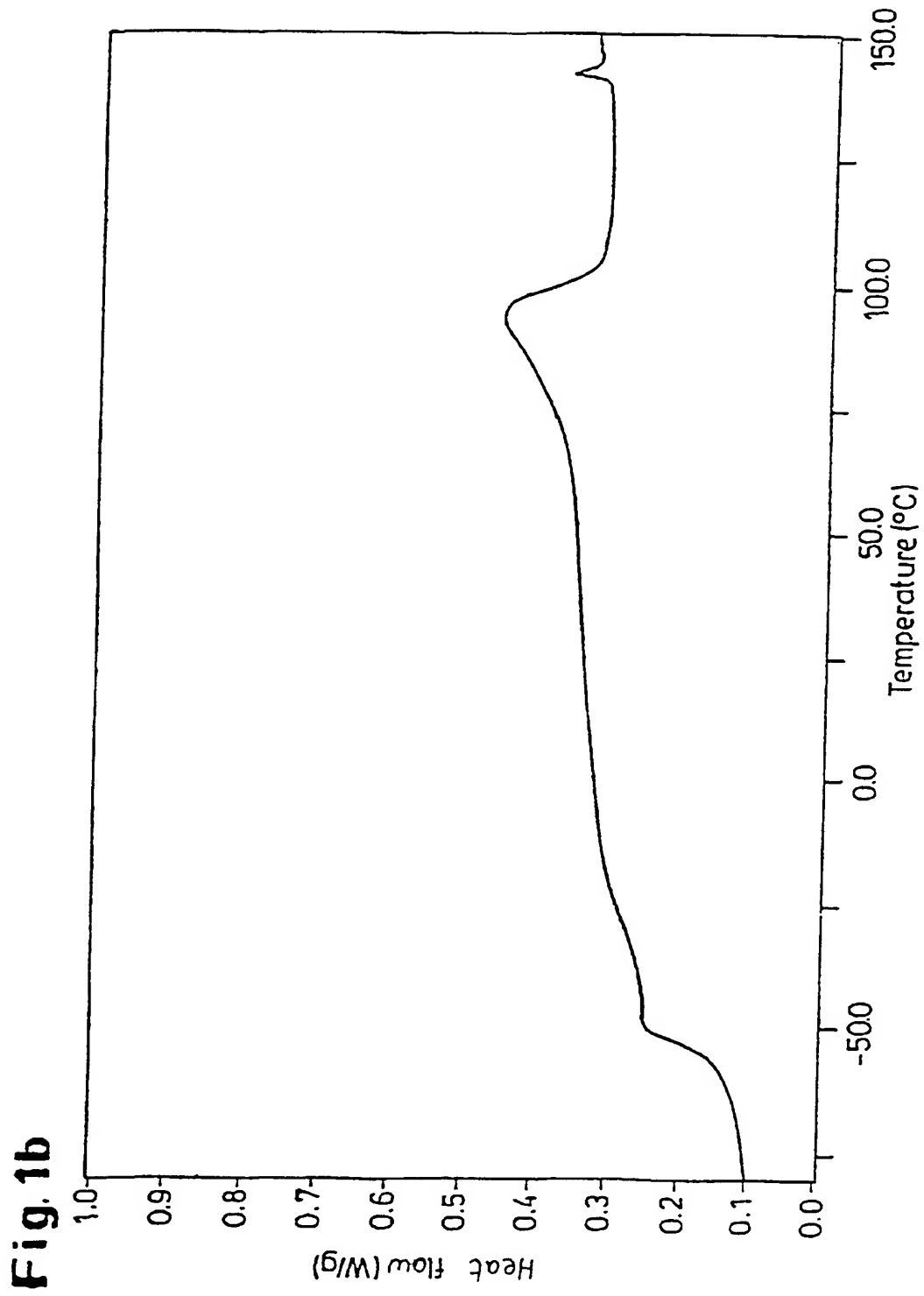
16.      Process according to Claim 1, characterized in that the half-intensity width of at least one melting peak is at most 30°C.

Fetherstonhaugh & Co.  
Ottawa, Canada  
Patent Agents

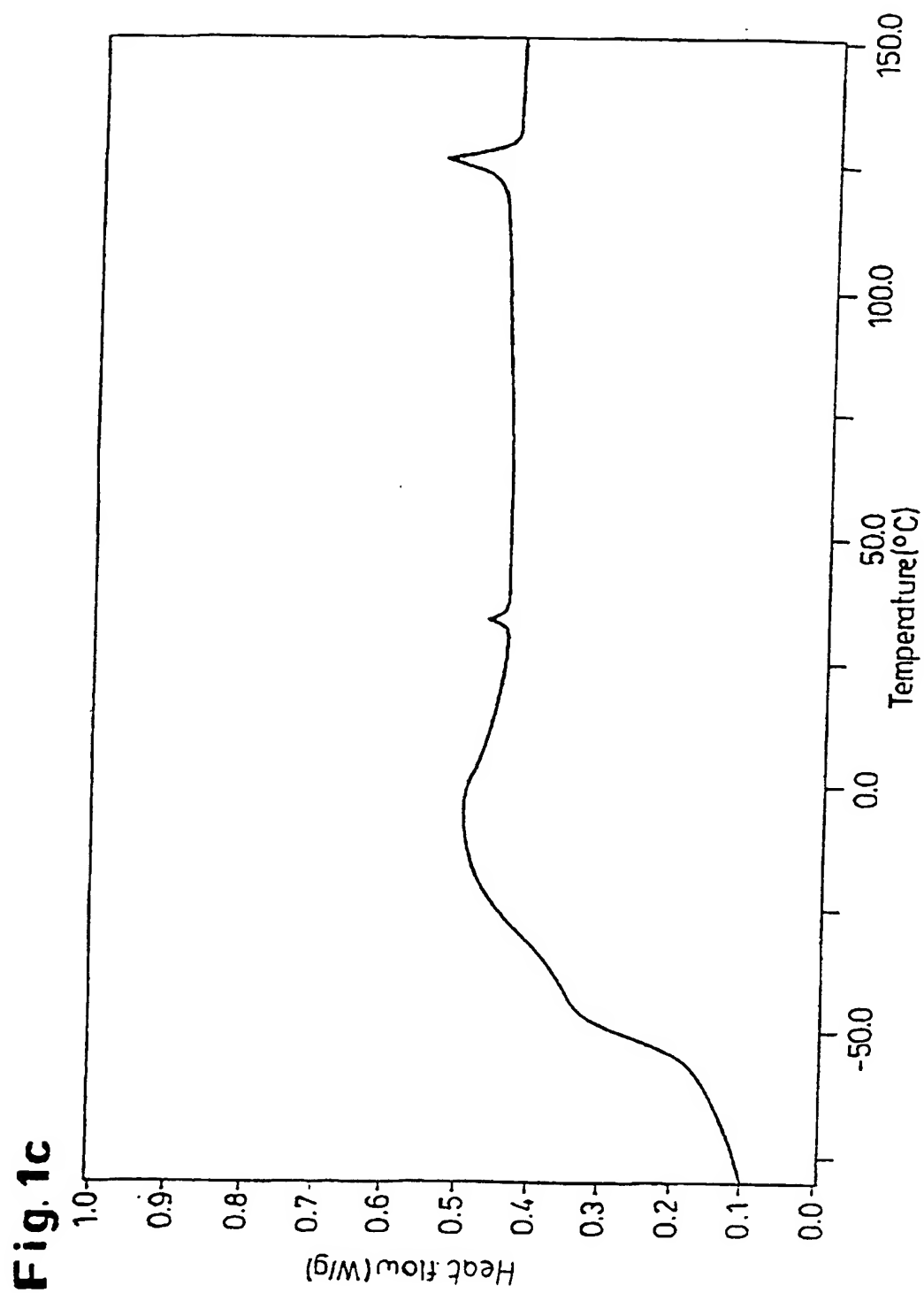
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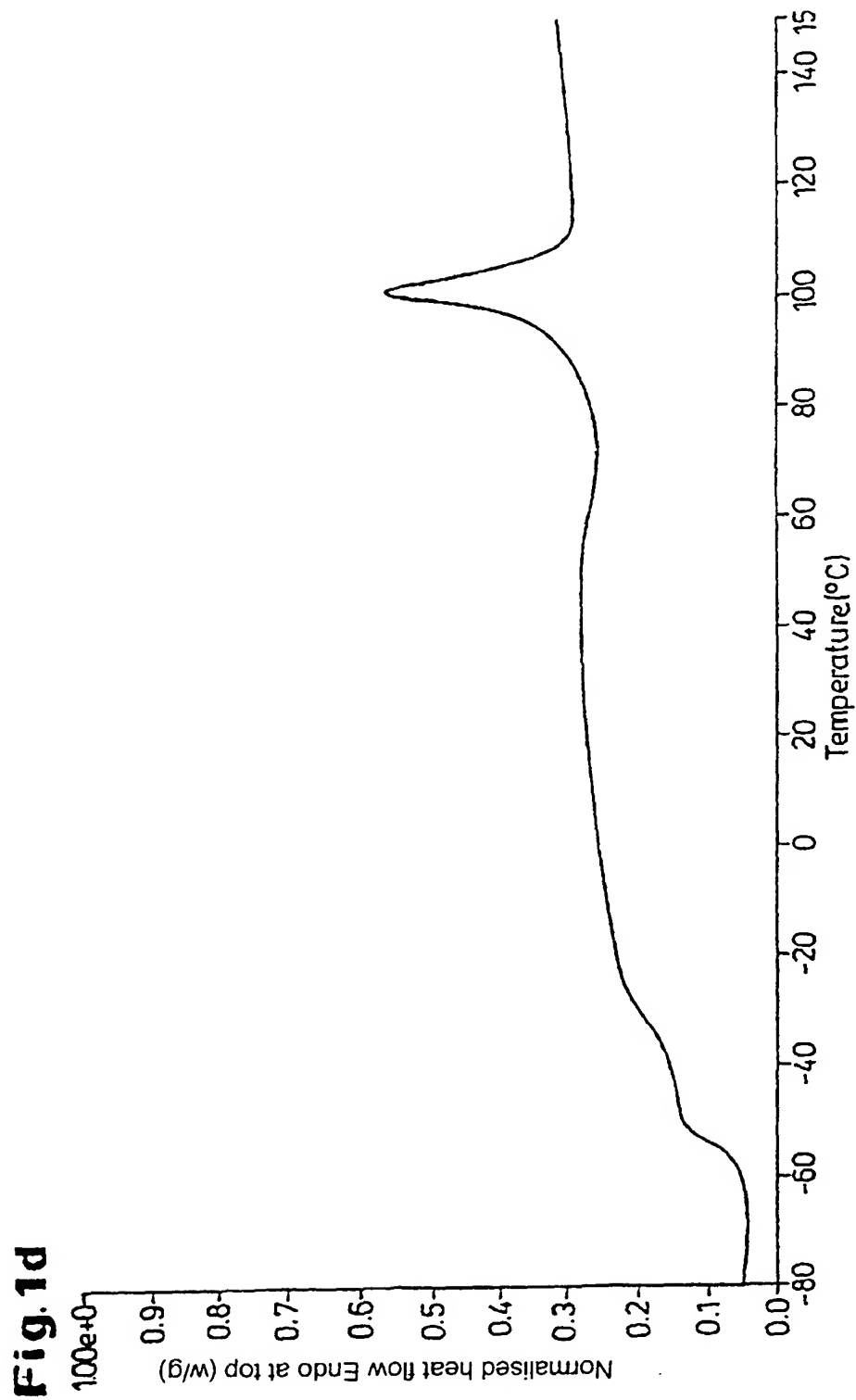
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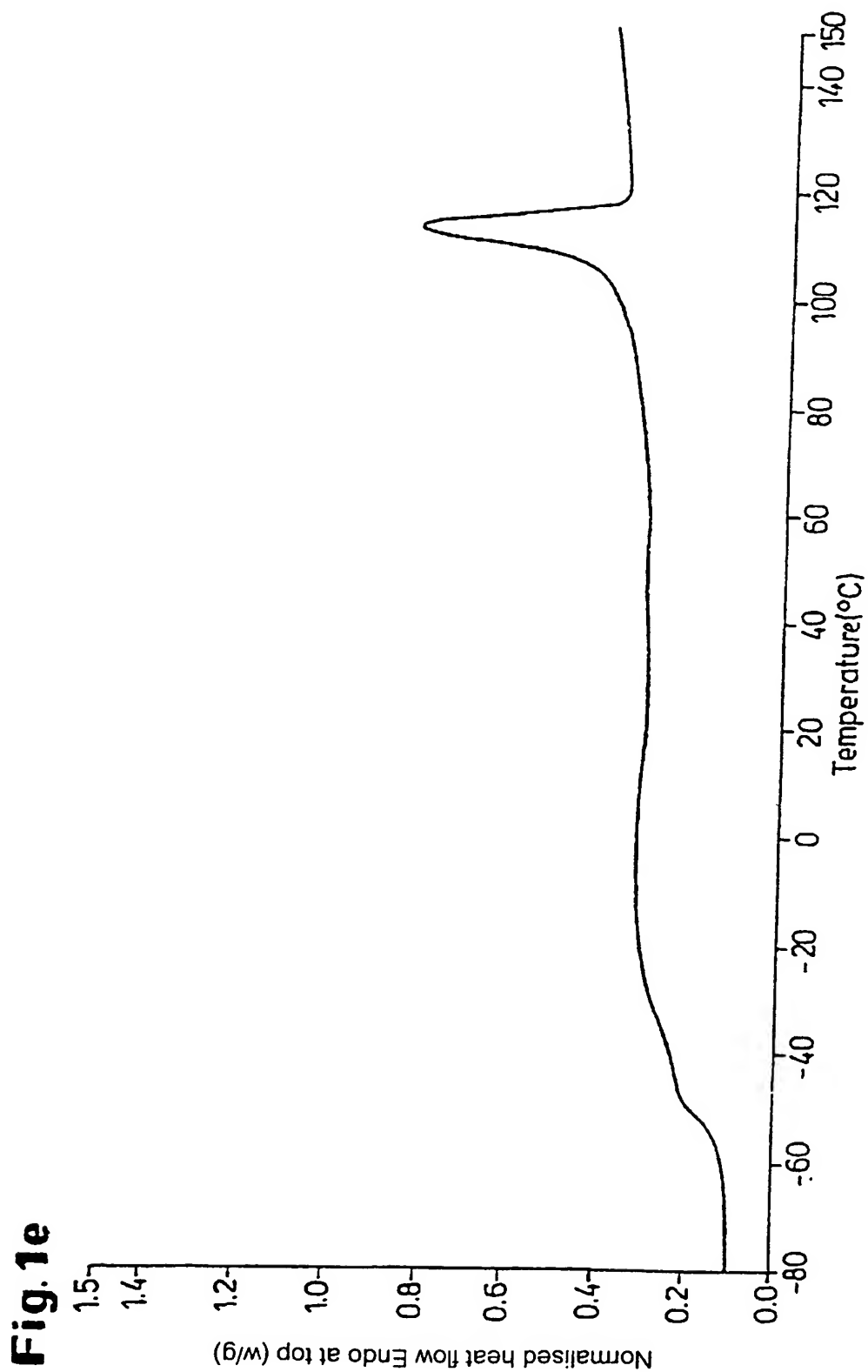
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